*Journal of the European Ceramic Society* **15** (1995) 1031–1035
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0955-2219/95/$9.50

0955-2219(95)00072-0

# Constitution of Porcelain Before and After Heat-Treatment. I: Mineralogical Composition

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(Received 2 February 1994; revised version received 8 July 1994; accepted 31 March 1995)

***Abstract***

*Porcelain compositions were prepared with and without the addition of mineralizers/nucleating agents and their phase assemblages were studied before and after subjecting them to heat-treatment. Mullite, quartz and glass were detected in the compositions before heat-treatment, but cristobalite appeared as an additional phase after heat-treatment. Heat-treated compositions were comparatively rich in mullite following crystallization from the glassy phase. $Nb_2O_5$ was the most efficient nucleating agent among those tried.*

## 1 Introduction

Porcelain is the vitrified product of mixtures of clay, quartz and feldspar, and chemical porcelain[1] is one such product having 60–65 wt% clay. Mullite and glass constitute the major phases[2] of porcelain which also contains some quartz,[3] cristobalite, tridymite and corundum are rarely found in it.

Although mullite is endowed with excellent mechanical, creep, thermal and chemical properties,[4] the electrical properties are not well studied. It has been shown in earlier work[5] that the electrical resistivity of porcelain decreases with increase in mullite content. The electrical resistivity of mullite depends on the $Al_2O_3:SiO_2$ molar ratio. While mullite of composition $2Al_2O_3.SiO_2$ (2 : 1 mullite) is an electrical insulator[6] comparable to siliceous phases,[7] the $3Al_2O_3.2Sio_2$ composition, i.e. 3 : 2 mullite has poor electrical resistivity especially above 1000°C.[6] The 2 : 1 mullite has a band gap energy 7·7ev,[6] but 3 : 2 mullite has a band gap energy 1·43 ev.[8,9] Mullite crystals in porcelain have $3Al_2O_3.2SiO_2$ composition as these are derived from the solid state decomposition of the clay component and are formed by nucleation and crystallization from the feldspathic glass.

It consequently seems possible to make porcelain more conducting by increasing its mullite content. This can be accomplished by promoting reaction between the residual quartz and glass in the presence of mineralizers, e.g. $Fe_2O_3$ or $TiO_2$ by a two step reaction,[10,11] *viz.* replacement of $Al^{3+}$ ion from glass by the cation of the mineralizer and subsequent diffusion of $Al^{3+}$ ion into the residual silica.

The glassy phase in the porcelain body lies mainly in the $Al_2O_3$–$SiO_2$ system and is prone to crystallization[12] to mullite. This needs incorporation of suitable oxides, such as $Fe_2O_3$, $TiO_2$ or $Cr_2O_3$ into the glass and subsequent heat-treatment of the nucleated glass.

The glass in porcelain contains alkalis ($K_2O$ + $Na_2O$) and when it is exposed to elevated temperatures, crystallization of cristobalite and tridymite phases[13] is also possible. These phases have high electrical resistivity and thereby counter balance the effect of mullite.

In the literature concerning semi-conductor and dielectric porcelain,[14] ceramic heating elements,[15,16] and glass-ceramic heating elements,[17] no mention is made of the constitution of these heating elements and its effect on electrical properties. It has, however, been observed[18] that a mullite porcelain body can be employed as a temperature indicator-cum-controller.

In the present work, chemical porcelain samples, with and without the addition of mineralizers/nucleants have been prepared and their constitution has been studied before and after subjecting them to heat-treatment. The mineralogical compositions (phase assemblages) of the porcelain samples are reported in this paper.

## 2 Experimental

### 2.1 Raw materials

The chemical analyses of the china clay, glass sand and potash feldspar are shown in Table 1. The porcelain samples were prepared from a mixture of clay (63 wt%), quartz (12 wt%) and feldspar (25 wt%).

**Table 1.** Chemical analyses of raw materials

| *Raw Material* | *Concentration (wt.%) of constituent oxides* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *$SiO_2$* | *$Al_2O_3$* | *$Fe_2O_3$* | *$TiO_2$* | *CaO* | *MgO* | *$K_2O$* | *$Na_2O$* | *LOI* |
| Clay | 45·2 | 39·1 | 0·65 | 0·22 | Trace | Trace | 0·38 | 0·03 | 14·82 |
| Quartz | 99·9 | — | — | — | — | — | — | — | — |
| Feldspar | 64·43 | 18·05 | 0·30 | Trace | 0·89 | Trace | 13·55 | 2·22 | 0·30 |

## 2.2 Mineralizers/nucleating agents

The transition metal oxides, $Fe_2O_3$, $TiO_2$, $Cr_2O_3$, $V_2O_5$ and $Nb_2O_5$ were incorporated into the basic composition individually to the extent of 2–8 wt% and also in combinations of ($V_2O_5$ + $TiO_2$) and ($V_2O_5$ + $Fe_2O_3$). The concentrations of the oxides are given in Table 2.

## 2.3 Sample preparation

A good casting slip was obtained by milling a mixture of clay, quartz and feldspar. Discs of 25 mm diameter × 6 mm height were cast, dried and fired in an electric furnace at 1400°C for 1 h followed by overnight cooling.

The mineralised compositions are obtained by incorporating the oxides into the base composition during milling.

## 2.4 Heat-treatment

The glassy phases in the porcelain samples resembled very closely feldspathic glass and a strong exothermic peak[11] characteristic of crystallization of mullite occurred in their DTA traces. This peak temperature (1150°C) was accepted as heat-treatment temperature for the 50 h duration for glass crystallization. This was carried out in an electric furnace with 10°C/min heating rate to 1150°C, held for 50 h and cooled overnight.

## 2.5 Identification and estimation of phases

The crystalline phases were identified and estimated by X-ray diffractometry. The quantity of glass was calculated by difference.

**Table 2.** Concentration (wt.%) of mineralizers/nucleating agents

| *Sample no.* | *Mineralizers/nucleating agents* | *Concentration (wt.%) of nucleating agents/ mineralizers* |
|---|---|---|
| 1 | — | — |
| 2 | $TiO_2$ | 8 |
| 3 | $V_2O_5$ | 3 |
| 4 | $Fe_2O_3$ | 2·6 |
| 5 | $TiO_2$ | 2·6 |
| 6 | ($V_2O_5$ + $Fe_2O_3$) | $V_2O_5$–1·5 + $Fe_2O_3$–1·3 |
| 7 | ($V_2O_5$ + $TiO_2$) | $V_2O_5$–1·5 + $TiO_2$–1·3 |
| 8 | $Cr_2O_3$ | 2·5 |
| 9 | $Nb_2O_5$ | 2 |

### 2.5.1 Crystalline phase

The identification was done in the usual manner from the peaks by running the diffractometer from 15–65° ($2\theta$) at 2° ($2\theta$)/min.

The quantitative analysis was done by the internal standard technique, NaF being the internal standard. Three calibration curves were drawn by scanning the zones ($2\theta$): 37–43° for mullite, 48–58° for quartz and 20·5–23·5° and 37·5–40·5° for cristobalite and by plotting the peak-height ratios against phase concentrations. The experimental samples were similarly scanned and concentrations of phases were computed from the calibration curves.

### 2.5.2 Glassy phase

The $SiO_2$ and $Al_2O_3$ in porcelain occur in mullite, quartz, cristobalite and in the glass formed in combination with the other oxides. Knowing the quantities of crystalline phases, the quantity and composition of the glass can be estimated.

The feldspathic matrix glass comprised $SiO_2$, $Al_2O_3$ and $K_2O$ to the extent of (90 ± 5) wt% in the samples before heat-treatment and (85 ± 5) wt% in the samples after heat-treatment.

## 3 Results

The concentrations of the crystalline and glassy phases in the samples before and after heat-treatment are compiled in Tables 3 and 4, respectively. Mullite and quartz were detected in all the samples whether heat-treated or not. Cristobalite was virtually absent in the samples before heat-treatment except the one containing $Nb_2O_5$. However, cristobalite appeared in all the samples after heat-treatment in sufficient quantity and mullite content also increased significantly.

The calculated chemical compositions of the glassy phases in the samples before and after heat-treatment are tabulated in Tables 5 and 6, respectively. These compositions can be represented in terms of their major constituents on the $SiO_2$–$Al_2O_3$–$K_2O$ ternary diagram.

It was observed that the compositions of glasses of almost all the samples before heat-treatment lie

Table 3. Mineralogical compositions of porcelain samples before heat-treatment

| Sample no. | Description | Concentration (wt.%) of phases | | | |
|---|---|---|---|---|---|
| | | Crystalline phases | | | |
| | | Mullite | Quartz | Cristobalite | Glassy Phase |
| 1B | B.C. | 32·7 | 4·5 | 0·2 | 62·6 |
| 2B | B.C. + 8% $TiO_2$ | 28·5 | 6·5 | 0 | 65·0 |
| 3B | B.C. + 3% $V_2O_5$ | 39·7 | 7·5 | 0·3 | 52·5 |
| 4B | B.C. + 2·6% $Fe_2O_3$ | 33·5 | 10·7 | 0 | 55·7 |
| 5B | B.C. + 2·6% $TiO_2$ | 33·5 | 3·0 | 0 | 63·5 |
| 6B | B.C. + (1·5% $V_2O_5$ + 1·3% $Fe_2O_3$) | 36·0 | 8·3 | 0·4 | 55·4 |
| 7B | B.C. + (1·5% $V_2O_5$ + 1·3% $TiO_2$) | 32·7 | 6·3 | 0·3 | 60·7 |
| 8B | B.C. + 2·5% $Cr_2O_3$ | 29·7 | 5·5 | 0·4 | 64·3 |
| 9B | B.C. + 2% $Nb_2O_5$ | 43·0 | 9·7 | 24·8 | 22·4 |

B.C. = Base Composition.

Table 4. Mineralogical compositions of porcelain samples after heat-treatment

| Sample no. | Description | Concentration (wt.%) of phases | | | |
|---|---|---|---|---|---|
| | | Crystalline phases | | | |
| | | Mullite | Quartz | Cristobalite | Glassy Phase |
| 1A | B.C. | 41·5 | 5·4 | 22·8 | 30·4 |
| 2A | B.C. + 8% $TiO_2$ | 35·5 | 3·7 | 27·8 | 33·0 |
| 3A | B.C. + 3% $V_2O_5$ | 43·0 | 5·7 | 28·6 | 22·6 |
| 4A | B.C. + 2·6% $Fe_2O_3$ | 41·5 | 6·2 | 25·2 | 27·2 |
| 5A | B.C. + 2·6% $TiO_2$ | 40·7 | 5·3 | 31·0 | 23·0 |
| 6A | B.C. + (1·5% $V_2O_5$ + 1·3% $Fe_2O_3$) | 43·0 | 5·6 | 25·6 | 25·8 |
| 7A | B.C. + (1·5% $V_2O_5$ + 1·3% $TiO_2$) | 43·0 | 5·7 | 27·0 | 24·3 |
| 8A | B.C. + 2·5% $Cr_2O_3$ | 43·0 | 5·0 | 24·4 | 27·6 |
| 9A | B.C. + 2% $Nb_2O_5$ | 42·3 | 5·0 | 29·0 | 23·7 |

in the ternary system within the mullite phase field but those of almost all the samples after heat-treatment are distributed within the tridymite phase and K–feldspar phase fields only.

## 4 Discussion

Mullite is the primary crystalline phase in the porcelain samples. The amount of clay that is present in the batch composition can provide 39·9 wt% (maximum) mullite and the maximum concentration of mullite to be available from the entire batch is 46·2 wt%. It is observed from Table 3 that the mullite content of all the samples before heat-treatment with the exception of the one with $Nb_2O_5$ was less than 39·9 wt%. This suggests that clay had been the only source of mullite in these samples. A small amount of mullite, about 3·1 wt%, in the $Nb_2O_5$ containing sample in excess of the theoretical clay-derived value originated from the glassy phase. This might be due to the highly charged $Nb^{5+}$ cation of $Nb_2O_5$ which is also a more efficient nucleating agent than the other oxides used. $Nb_2O_5$ showed remarkable efficiency by effecting crystallization of mullite in considerable amount from the glassy phase within an hour of initial firing of the sample at 1400°C. The mullite content (43 wt%) of this sample almost reached the theoretical value. The $V^{5+}$ ion of $V_2O_5$ was almost equally efficient.

The other nucleating agents also enhanced mullite formation. Higher concentration of $TiO_2$, however, reduced mullite content of the base compositions as also found with $Cr_2O_3$. $TiO_2$ being a fluxing agent and growth inhibitor retarded mullite formation at higher concentration but at lower concentration improved mullitization by producing a little amount of liquid phase that assisted decomposition of clay to mullite. Due to its refractory nature $Cr_2O_3$ failed to provide a liquid phase and thereby the mullite content of the $Cr_2O_3$-containing sample dropped. Small amounts of $Fe_2O_3$ and combinations of ($Fe_2O_3$ + $V_2O_5$) or ($TiO_2$ + $V_2O_5$) also favoured more mullite formation in these samples by generating liquid phase.

**Table 5.** Compositions of glassy phases in porcelain samples before heat-treatment

| *Sample no.* | *Description* | *Concentrations (wt.%) of constituent oxides* | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | $CaO$ | $MgO$ | $K_2O$ | $Na_2O$ | $V_2O_5$ | $Cr_2O_3$ | $Nb_2O_5$ |
| 1B | B.C. | 77.28 | 13.82 | 0.86 | 0.25 | 0.39 | Trace | 6.36 | 1.02 | — | — | — |
| 2B | B.C. + 8% $TiO_2$ | 64.70 | 15.85 | 0.72 | 12.13 | 0.33 | Trace | 5.40 | 0.86 | — | — | — |
| 3B | B.C. + 3% $V_2O_5$ | 77.60 | 6.54 | 0.94 | 0.28 | 0.44 | Trace | 7.13 | 1.13 | 5.90 | — | — |
| 4B | B.C. + 2·6% $Fe_2O_3$ | 71.76 | 13.84 | 5.83 | 0.27 | 0.41 | Trace | 6.79 | 1.08 | — | — | — |
| 5B | B.C. + 2·6% $TiO_2$ | 75.03 | 12.23 | 0.81 | 4.60 | 0.37 | Trace | 6.00 | 0.95 | — | — | — |
| 6B | B.C. + (1·5% $V_2O_5$ + 1·3% $Fe_2O_3$) | 74.40 | 10.83 | 3.35 | 0.27 | 0.42 | Trace | 6.82 | 1.08 | 2.82 | — | — |
| 7B | B.C. + (1·5% $V_2O_5$ + 1·3% $TiO_2$) | 72.92 | 13.56 | 0.84 | 2.48 | 0.38 | Trace | 6.24 | 0.99 | 2.59 | — | — |
| 8B | B.C. + 2·5% $Cr_2O_3$ | 71.52 | 16.10 | 0.80 | 0.24 | 0.36 | Trace | 5.94 | 0.94 | — | 4.09 | — |
| 9B | B.C. + 2% $Nb_2O_5$ | 63.43 | 5.33 | 2.15 | 0.64 | 0.98 | Trace | 16.05 | 2.55 | — | — | 8.85 |

**Table 6.** Compositions of glassy phases in porcelain samples after heat-treatment

| *Sample no.* | *Description* | *Concentrations (wt.%) of constituent oxides* | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $TiO_2$ | $CaO$ | $MgO$ | $K_2O$ | $Na_2O$ | $V_2O_5$ | $Cr_2O_3$ | $Nb_2O_5$ |
| 1A | B.C. | 73·91 | 7·86 | 1·75 | 0·52 | 0·80 | Trace | 13·07 | 2·08 | — | — | — |
| 2A | B.C. + 8% $TiO_2$ | 49·76 | 15·97 | 1·28 | 21·37 | 0·58 | Trace | 9·52 | 1·51 | — | — | — |
| 3A | B.C. + 3% $V_2O_5$ | 61·05 | 5·06 | 2·05 | 0·61 | 0·93 | Trace | 15·25 | 2·42 | 12·61 | — | — |
| 4A | B.C. + 2·6 $Fe_2O_3$ | 64·10 | 7·94 | 11·33 | 0·53 | 0·81 | Trace | 13·20 | 2·10 | — | — | — |
| 5A | B.C. + 2·6% $TiO_2$ | 56·24 | 11·28 | 2·06 | 11·74 | 0·94 | Trace | 15·31 | 2·43 | — | — | — |
| 6A | B.C. + (1·5% $V_2O_5$ + 1·3% $Fe_2O_3$) | 65·72 | 4·56 | 6·74 | 0·55 | 0·84 | Trace | 13·72 | 2·18 | 5·69 | — | — |
| 7A | B.C. + (1·5% $V_2O_5$ + 1·3% $TiO_2$) | 63·79 | 4·81 | 1·95 | 5·75 | 0·89 | Trace | 14·49 | 2·30 | 6·00 | — | — |
| 8A | B.C. + 2·5% $Cr_2O_3$ | 68·44 | 4·34 | 1·75 | 0·52 | 0·80 | Trace | 13·06 | 2·08 | — | 9·00 | — |
| 9A | B.C. + 2% $Nb_2O_5$ | 63·19 | 7·12 | 2·05 | 0·61 | 0·93 | Trace | 15·25 | 2·43 | — | — | 8·42 |

The glassy phase of the samples before heat-treatment contained 10–30 wt% $Al_2O_3$ (Table 5) and aluminosilicate glass of similar $Al_2O_3$ content could be suitably nucleated and crystallized[12] to mullite by heat-treatment. Moreover, the compositions of glass in the samples before heat-treatment exist within the mullite phase field. These criteria strongly favoured the separation of mullite from the glassy phase in these samples and this fact was supported by the results presented in Table 3 and Table 4. The mullite content of each sample in Table 4 exceeded the amount which was available from its clay component only.

The glass compositions of the samples after heat-treatment became more siliceous (Table 6) and entered the tridymite and K–feldspar zones. Good amount of cristobalite also appeared here. By virtue of their low $Al_2O_3$ and high $K_2O$ content, these glassy phases almost reached mineralogically stable state but longer heat-treatment might cause microstructural changes in the samples.

## 5 Conclusions

(1) The glassy phase in porcelain is prone to nucleation and crystallization by incorporation of metal oxides and heat-treatment.

(2) Mullite content of porcelain can be increased by 6–7 wt%: over that is theoretically available from the clay component only.

(3) Cristobalite precipitates out along with mullite by heat-treatment.

## Acknowledgements

The authors wish to thank Dr B. K. Sarkar, Director of the Institute, for his permission to publish the paper. One of the authors (P.S.) is grateful to CSIR, India for providing him with a research fellowship to carry out this study.

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