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Effect of pyrophyllite on vitrification and on physical properties of triaxial porcelain

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Abstract

Quartz was progressively replaced by pyrophyllite in a conventional porcelain mix with a composition of 50% clay, 25% quartz and 25% feldspar. The addition resulted in early vitrification and decreased thermal expansion of the sintered specimen. Addition of up to 15% pyrophyllite decreased the fired shrinkage by 6% and improved the fired strength by around 29% compared to the standard body. The gradual increase in flexural strength with incorporation of pyrophyllite was primarily due to the elimination of stresses in the structure with a decreasing quartz content as well as to the increasing amount of secondary mullite distributed throughout the matrix forming an interlocking network. However, the firing temperature and the generation of the correct amount of properly sized mullite needles are vital in achieving the desired strength. Pyrophyllite was found to dissolve in the melt in preference to quartz. Beyond the optimum proportion of pyrophyllite, a large volume of glass formed as well as large elongated pores distributed in the matrix resulting in deterioration of mechanical properties.

Keywords: B. Microstructure; D. Porcelain; Pyrophyllite; Quartz; Vitrification

1. Introduction

Triaxial white ware body essentially consists of 50% kaolinite clay, 25% quartz and 25% feldspar. Although quartz plays a significant role in the development of ultimate properties of the product as well as appropriate microstructure, only a small portion of it gets dissolved in the melt during firing while a significant amount remains unreacted. The unreacted quartz phase undergoes transformations during cooling and the resultant volume change leads to the development of stresses in the structure which adversely affects the mechanical strength as well as thermal shock resistance [1]. Chaudhuri [2] observed that thermal shock resistance of hard porcelain deteriorated with the increasing amount of quartz and glassy matrix while the same improved with increasing mullite content. The temperature at which quartz begins to dissolve and interact with surrounding materials is strongly affected by batch composition as well as particle size of quartz [3–5]. Cracks are commonly observed in and around quartz grains with sizes >20 μm resulting from large thermal expansion mismatch between crystalline quartz ($\alpha = 23 \times 10^{-6}\ \mathrm{K}^{-1}$) and the glassy phase ($\alpha = 3 \times 10^{-6}\ \mathrm{K}^{-1}$) in the temperature range 20–750 °C [4,6]. The stresses in the glassy phase create tensile force perpendicular and compressive force parallel to the grain boundaries [7]. Highest dissolution of quartz in the melt will reduce the tensile force between residual quartz and surrounding glassy phase [8].

Mullite is the only stable phase in the Al_2O_3–SiO_2 system at atmospheric pressure. The mullite phase is believed to play a significant role in the development of traditional and advanced ceramics [9,10]. Lieberman [11] observed that replacement of quartz by aluminium oxide in an electrical porcelain composition resulted in 100% increase in flexural strength. He correlated the increase in strength with the amount of mullite and corundum as well as the decrease in the number of micro cracks. Khandelwal and Cook [12] achieved 200% increase in transverse strength by adding 40% alumina to a vitreous china body. Increasing alumina

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and decreasing feldspar content increased the total crystalline content of the fired body [12]. Analysis of microstructures revealed a higher mullite content. Increased interlocking of the mullite crystals is thought to increase thermal shock resistance. On the other hand the same author compared the strength of two quartz bodies with different mullite contents and opined that it was not the mullite content but the microstructure (the quantity, size, size distribution and shape of various constituent phases) contributed significantly in the development of porcelain properties. Tkalcec et al. [13] observed that addition of talc up to 4% increased the quantity of mullite but reduced the MOR due to the increase in the quantity and size of pores in the fired bodies. Maiti and Kumar [14] observed that progressive replacement of quartz by sillimanite sand in a porcelain composition resulted in increased flexural strength and fracture toughness. Prasad et al. [15] replaced quartz and feldspar in a white ware composition with sericitic pyrophyllite ($K_2O + Na_2O$ 10.08%). Incorporation of 22.5% sericitic pyrophyllite resulted in increased fired strength while decreasing the thermal expansion. This was attributed to the presence of spherical shaped pores and the decrease in free quartz content. In another work of Bhasin et al. [16], the effect of pyrophyllite additions on sintering characteristics of fly ash-based ceramic wall tiles was studied. The impact strength and apparent density was found to increase with the increase in pyrophyllite content while decreased water absorption values were observed. Further, presence of pyrophyllite imparted improved thermal shock resistances. Rieger [17] observed that high-sericitic pyrophyllite has the ability to form mullite at comparatively low temperatures and interlocking grain structure of mullite results in greatly increased fired strength in vitrified bodies. In addition, high sericitic pyrophyllite also has the advantage of low-moisture expansion bodies, little shrinkage, and less warpage.

In the present study, quartz was progressively replaced by pyrophyllite in a normal porcelain white ware composition consisting of 50% clay, 25% feldspar and 25% quartz. Effect of such substitution on shrinkage, bulk density, porosity, thermal expansion, strength, phase evolution in relation to firing temperature was studied. Some selected samples were examined for micro-structural changes.

2. Experimental

The raw materials used in this investigation were china clay (Rajmahal, Bihar, India), plastic clay (Ranchi, Jharkhand, India), quartz, feldspar and pyrophyllite (Maharashtra, India).

The chemical analysis of the raw materials conducted by standard method is given in Table 1.

Batch (Table 2) was wet ground for 16 h in porcelain jars with porcelain balls up to a fineness of around 53 μm. The ground slurry was sieved, passed through a permanent magnet, dewatered and test specimens were extruded in a vacuum extruder in cylinders of 2 cm in diameter and 15 cm in length. The test specimens were dried and subsequently fired between 1150 and 1300 °C in an electric furnace with 2 h soaking at the respective peak temperatures.

Table 1
Chemical analysis of raw materials (wt.%)

Constituency	Pyrophyllite	China clay	Plastic clay	Quartz	Feldspar
SiO_2	59.51	48.87	58.38	98.11	66.81
TiO_2	0.26	0.93	1.15	Trace	Trace
Al_2O_3	30.43	34.39	25.54	0.41	18.08
Fe_2O_3	0.86	0.87	0.49	0.22	0.24
CaO	0.37	1.42	0.95	0.68	1.03
MgO	0.78	Trace	Trace	Trace	0.23
Na_2O	0.73	0.10	0.13	0.15	1.69
K_2O	1.95	0.23	0.63	0.07	10.94
LOI	5.40	12.83	12.24	0.19	0.58

Apparent porosity and bulk density of the specimens fired at different temperatures were measured by the water displacement method. Flexural strength in three-point bending stress was measured with an electromechanical universal tester (Instron 1195). The cross head speed was 1 mm/min and a span of 100 mm was maintained throughout the experiment. Flexural strength was measured using the formula = 8 $WL/\Pi D^3$, where W is the breaking load, L the span length, D the diameter of the cylindrical specimens.

Linear thermal expansion of the matured specimens was determined using an Orton Automatic Dilatometer (Bosch & Lamb, UK) at a heating rate of 2 K/min.

Major crystalline phases present in the matured specimens were identified by X-ray diffraction (XRD) using a Philips PW-1730 X-ray diffractometer. Microstructure was studied by SEM analysis on selected sintered samples using a LEO S-430i apparatus.

Concentration of crystalline phases was estimated by X-ray diffractometry in a Philips make X-pert Pro diffraction unit attached with secondary monochromator automatic divergence slit and Ni-filter was used to get monochromatic Cu Kα radiation. The instrument was run in step scan mode with step size (0.02) and time per step 8 s/step within the angle 5–75°. The collected data were refined using profit software. X-Pert plus and Quaser software based on Rietveld were used to calculate the percentage of mullite and quartz phases where standard mullite and quartz were used as reference materials.

Table 2
Body composition with progressive replacement of quartz with pyrophyllite (%)

Composition	China clay	Plastic clay	Feldspar	Quartz	Pyrophyllite
S-1	25	25	25	25	0
S-2	25	25	25	20	5
S-3	25	25	25	15	10
S-4	25	25	25	10	15
S-5	25	25	25	5	20
S-6	25	25	25	0	25

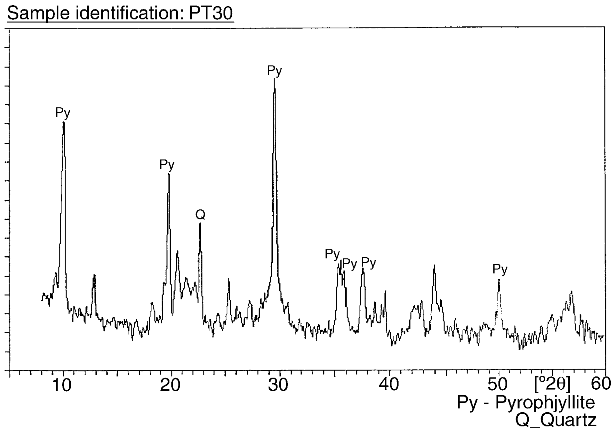

Fig. 1. XRD analysis of pyrophyllite.

3. Results and discussion

The chemical analysis (Table 1) shows that clay, quartz and feldspar used in the present study were of the common type. SiO_2 and Al_2O_3 are the major constituents with low Fe_2O_3 and alkali ($K_2O + Na_2O$) content. The XRD pattern of pyrophyllite (Fig. 1) shows, in addition to the presence of pyrophyllite as the major phase, some quartz inclusions. The oxide composition of all the experimental bodies is given in Table 3. Fig. 2 shows that up to 1200 °C fired shrinkage increased with increasing pyrophyllite content and beyond this temperature the reverse trend was observed. The curve for apparent porosity (Fig. 3) of specimens fired at 1250 °C indicated a sharp drop from 4.75% (S-1) to 0.16% (S-3) and the value remained more or less constant with progressive incorporation of pyrophyllite up to 15%. Thus, quartz by pyrophyllite replacing in a standard whiteware body resulted in lowering its vitrification temperature and may be of particular interest in the modern day technology for energy conservation. Decrease in porosity with temperature for any triaxial porcelain composition due to more glass formation is a common phenomenon. However, addition of pyrophyllite (which does not contain much alkali) in the present study decreased the porosity which is probably due to formation of dense, interlocked structure during vitrification. This has also been observed by Bhasin et al. [16].

Table 3
Oxide composition of the different compositions (wt.%)

	Composition					
	S-1	S-2	S-3	S-4	S-5	S-6
SiO_2	72.235	70.525	68.765	67.005	65.245	63.485
TiO_2	0.60	0.61	0.63	0.64	0.66	0.67
Al_2O_3	21.88	23.48	25.08	26.68	28.28	29.88
Fe_2O_3	0.51	0.53	0.55	0.57	0.59	0.61
CaO	1.11	1.15	1.10	1.05	1.00	0.95
MgO	0.06	0.14	0.17	0.20	0.23	0.26
Na_2O	0.53	0.55	0.58	0.61	0.64	0.67
K_2O	3.03	3.13	3.23	3.33	3.43	3.53

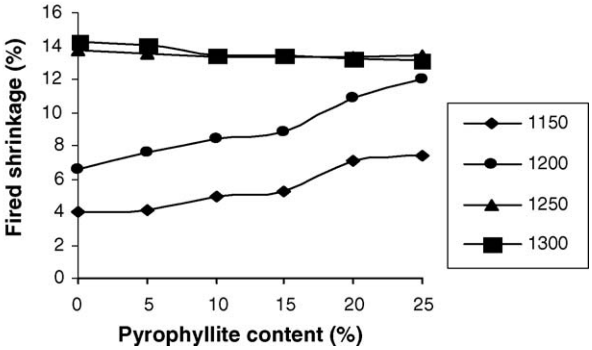

Fig. 2. Effect of pyrophyllite content on fired shrinkage at different temperatures.

XRD analysis indicated appreciable mullite formation even at 1150 °C. The fluxing action of feldspar associated with amorphous silica from clay relicts during meta-kaolin formation facilitated crystallization of mullite in the early stage of firing than in pure clay body. SEM analysis of S-1 (Fig. 6) revealed two different types of mullite; feldspar-penetrated clay relicts containing primary granular type mullite and a matrix of clay feldspar and quartz containing elongated and acicular type mullite (smaller proportion) in agreement with Iqbal and Lee [18]. The proportion of acicular mullite increased as quartz was gradually replaced by pyrophyllite. Figs. 8 and 9 (SEM of S-3 and S-4, respectively) showed well-formed needle-shaped secondary mullite forming a network throughout the microstructure. The observed variation in the morphology and size of mullite crystals may be explained by the gradient in viscosity of the relevant matrix and subsequent more rapid mass transport [19]. Mullite formation and its distribution in the feldspar and clay relicts is determined by concentration gradients as well as the diffusion rates of K_2O and Al_2O_3 [18]. Table 3 indicated that as pyrophyllite gradually replaced quartz in the mixes, total alkali ($Na_2O + K_2O$) and Al_2O_3 content increased progressively while there was a gradual decrease in the SiO_2 content. Again, as more and more pyrophyllite is incorporated in the compositions, the pyrophyllite gets dissolved in the feldspathic melt in

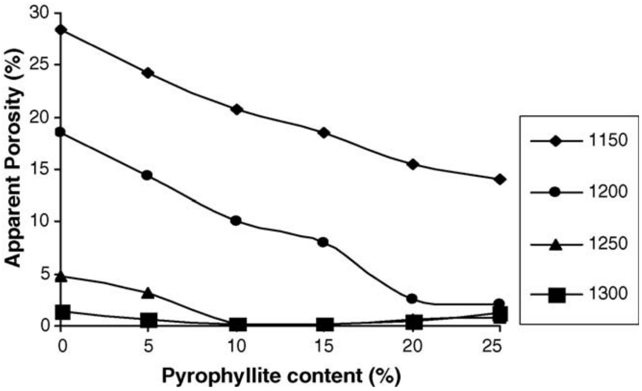

Fig. 3. Effect of pyrophyllite content on apparent porosity at different temperatures.

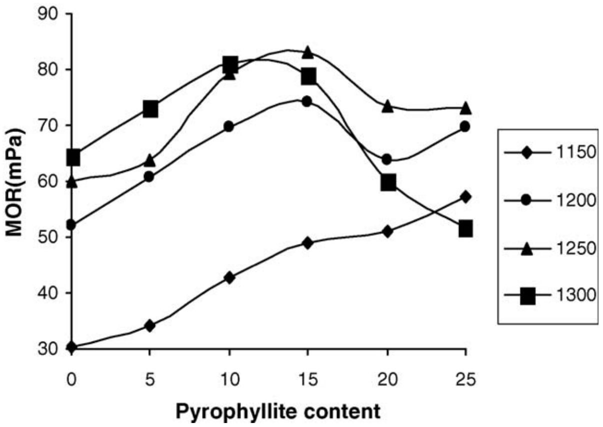

Fig. 4. Effect of pyrophyllite content on MOR at different temperatures.

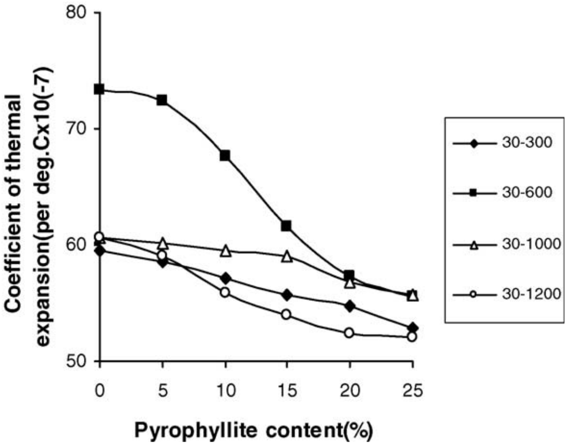

Fig. 5. Effect of pyrophyllite content on coefficient of thermal expansion of matured specimen at different range of temperatures.

preference to quartz (being more inert) and the viscosity of the resultant glass decreased. Formation and recrystallization of acicular type secondary mullite are therefore facilitated in the compositions containing higher proportion of pyrophyllite and this is confirmed in Table 4. As more and more alkali diffused out of feldspar with increasing temperature, the viscosity of the melt decreased and this facilitated secondary mullite to nucleate and grow. The relatively higher proportion of mullite and its well-developed interlocking network structure distributed throughout the matrix in the specimens S-3 and S-4 (Figs. 8 and 9) contribute significantly to the development of flexural strength (Fig. 4) as well as in the lowering in the coefficient of thermal expansion (Fig. 5). Here it may be mentioned that mechanical strength of the sintered specimens was also found to increase up to 15% pyrophyllite content, reaching a value of >80 MPa at 1250 °C. This phenomenon was also observed by Prasad et al. [15]. The coefficient of thermal expansion was also found to be strongly dependent on pyrophyllite content with the value decreasing with the increase in pyrophyllite content. Phase analysis of the sintered specimens (Table 4) indicated progressive increase in mullite content, again up to 15% pyrophyllite and thereafter it attain more or less constant value conforming to the observations of Sosman [20], Rado [21] and Iqbal and Lee [22]. The microstructure analysis of S-1 and S-2 (Figs. 6 and 7) further revealed that quartz grains were rather angular in nature while the grains tend to become round in specimens with decreasing quartz content. As the relative proportion of quartz content decreased from S-1 to S-6, the grains are expected to react more intensely with the feldspathic melt resulting in rounding of the edges as well as diminishing in size (Figs. 8 and 9). The wide solution rim around quartz grains showed their extensive dissolution and this rim formation increased with decreasing quartz content.

Table 4
Phase analysis (wt.%) of specimens of the different compositions fired at 1250 °C

Composition	Mullite	Quartz	Glass
S-1	15.5	29.4	55.4
S-2	15.1	25.0	59.9
S-3	18.2	19.1	62.7
S-4	20.0	16.3	63.7
S-5	18.3	13.1	68.6
S-6	16.2	10.6	73.2

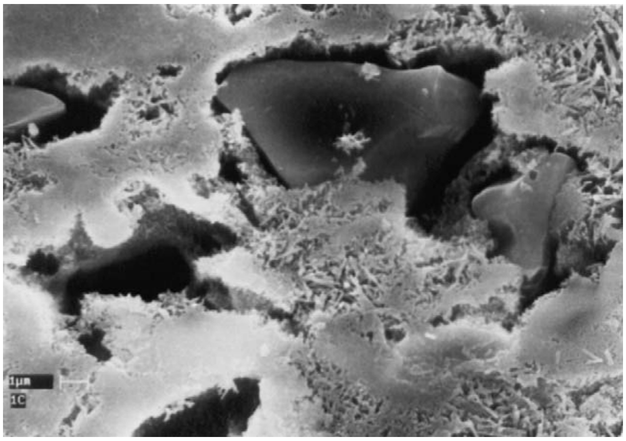

Fig. 6. SEM of composition S-1.

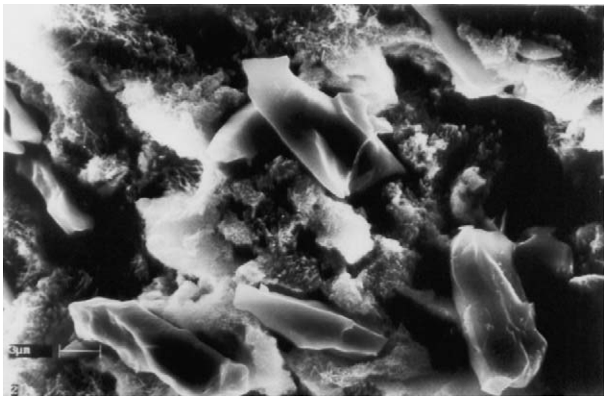

Fig. 7. SEM of composition S-2.

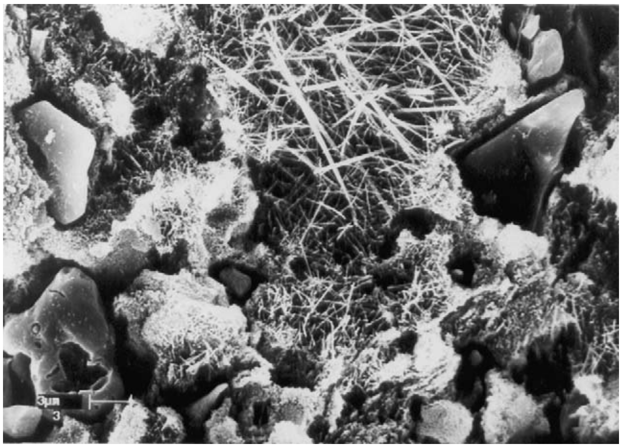

Fig. 8. SEM of composition S-3.

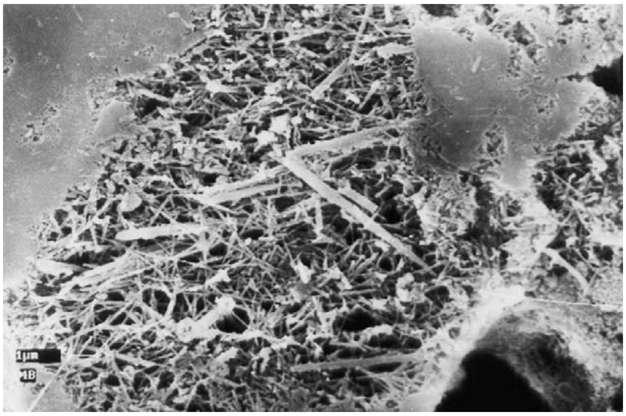

Fig. 9. SEM of composition S-4.

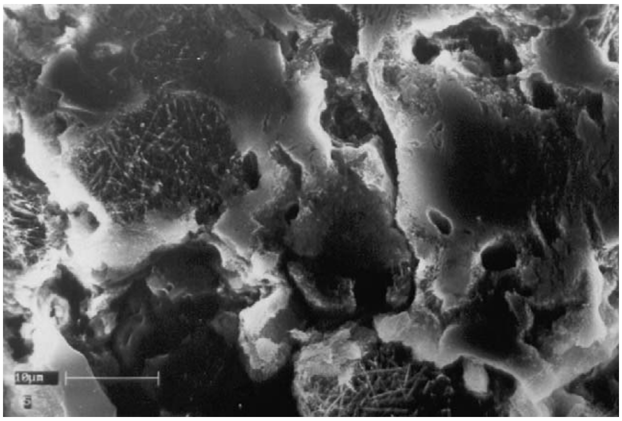

Fig. 10. SEM of composition S-5.

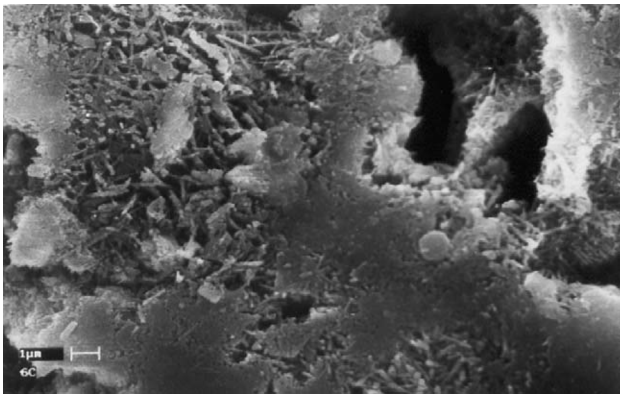

Fig. 11. SEM of composition S-6.

Fracturing was observed in quartz grains (internal and peripheral fracture) of larger sizes. As temperature went beyond 1250 °C, the mullite needles possibly coarsen, leading to a smaller number of large needles. These did not interlock as efficiently as the small ones, resulting in decreased strength [19]. Hence, firing temperature and generating the correct amount of properly sized mullite needles are vital in achieving the desired strength. Figs. 10 and 11 indicated large volume of glass formation in the specimens S-5 and S-6 which supported the results of Table 4. Large and elongated pores were found in the specimen S-5. The pores were also not uniformly distributed in the microstructure. Table 5 indicates that the glassy phase of S-5 was more viscous than that of S-1 due to the presence of higher Al_2O_3 and lower alkali content in the former. Due to an increase in viscosity of the glassy phase, there is a delay in the homogenization of the texture and this might be the reason for the elongated nature of the pores as well as their larger size. In comparison, the pores were found smaller in size in S-1 (Fig. 6). Figs. 10 and 11 indicated the presence of both primary and secondary mullite. Primary mullite formed in the specimens of S-5 and S-6 is not attacked by the melts low in silica and this conformed to the observations of Schueller [23] and Rado [21] who indicated that only melts high in silica dissolve mullite during firing.

Table 5
Calculated composition of probable glassy phase present in different compositions (wt.%) (considering mullite as $3Al_2O_3 \cdot 2SiO_2$)

Composition	SiO_2	Al_2O_3	$Na_2O + K_2O$	CaO	MgO	Fe_2O_3	TiO_2
S-1	69.89	19.36	6.39	2.16	0.20	0.92	1.08
S-2	68.76	21.06	6.13	1.92	0.23	0.88	1.02
S-3	70.91	19.12	6.07	1.75	0.27	0.88	1.00
S-4	70.65	19.31	6.18	1.65	0.31	0.89	1.00
S-5	68.42	22.05	5.93	1.46	0.33	0.86	0.96
S-6	65.95	24.91	5.73	1.30	0.35	0.83	0.91

4. Conclusions

Incorporation of pyrophyllite as a progressive replacement of quartz in a porcelain composition resulted in early vitrification. This also resulted in substantial reduction in the thermal expansion due to development of interlocking mullite needles. Addition of pyrophyllite reduced fired shrinkage and improved the flexural strength compared to the standard body. This was primarily due to the elimination of stresses in the structure with decreasing quartz content as well as due to presence of the feltlike interlocking of fine mullite needless in higher proportions. Mullite was found even at 1150 °C and its amount increased up to 1250 °C before decreasing at higher temperature. Beyond some optimum proportion of pyrophyllite (in this study 15%) there occur a large volume of glass formation and large elongated pores non-uniformly distributed in the microstructure which resulted in deterioration of the mechanical properties. The amount of closed pores in the specimens with pyrophyllite content beyond 15% and fired at 1300 °C was found to increase very abruptly which in turn is expected to increase the mean free fracture path per unit volume resulting in a decrease in strength.

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