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A new porcelainised stoneware material based on anorthite

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Abstract

The aim of the present study is to design and develop an alternative composition for making porcelainised stoneware, which has better properties than the conventional porcelainised stonewares. Contrary to the conventional porcelainised stonewares, this new body is designed to develop basically anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) crystals in the microstructure and to have a high crystalline to glassy phase ratio, after processing at 1200–1225 °C temperature ranges. To obtain the anorthite crystals, wollastonite, calcined alumina, quartz, Ukranian Ball Clay and some magnesia were used as raw materials. Technological properties, such as density, water absorption, firing shrinkage, flexural strength, thermal expansion behaviour and aesthetical properties were measured. X-ray diffraction (XRD) and scanning electron microscopy (SEM) studies were also carried out to analyse the microstructure. It was found that anorthite based material enables all the porcelainised stoneware requirements to be met and the material contains approximately 70% crystalline and 30% glassy phases. The flexural strength, 110 MPa, was two times higher than that of the conventional materials.

Keywords: Anorthite; Strength; Stoneware; Tiles; Silicates

1. Introduction

A new ceramic composition, which is based on anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) crystal formation, has been formulated to have a potential to be used as a porcelainised stoneware material. Porcelainised stoneware material is defined as extremely hard, highly dense, impervious (with water absorption of 0.5% or less) and unglazed vitrified ceramic which is obtained by fast firing, in the 1200–1230 °C temperature range, from a green pressed ceramic body.[1–3] It is possible to produce these tiles as imitations of stones such as granite, marble, sandstone, travertine, etc. with versatile and modern characteristics similar to those of natural stones.[4] The porcelainised stoneware tiles have been used for some time as a flooring and covering material in constructions. The material conception of porcelainised stoneware tiles in the ceramic sector started in the 1980s and especially over the last decade, due to the improved mechanical properties and aesthetic appearance, the ceramic tile industry has progressively shifted its production towards porcelainised stoneware tiles. This has attracted the attention of many scientists and technologists and many efforts are being made to produce the porcelainised stoneware tiles with improved properties and make uses of alternative raw material sources.

A typical stoneware body consists of SiO_2 and Al_2O_3 as major oxides and CaO, MgO, Na_2O, K_2O, and ZrO_2 as minor compounds. For supplementing these compounds, the raw materials are selected from a group of plastic and non-plastic minerals. Porcelainised stonewares are conventionally made with clay, feldspar and quartz, heat-treated to form a mixture of glass and crystalline phases.[4–7] Typical microstructure of the most common porcelainised stoneware bodies composed on average of 55–65 wt.% amorphous phase, 20–25 wt.% quartz and 12–16 wt.% mullite.[4,5] Moreover, small quantities of corundum and/or zircon may also be added for the purpose of stabilising certain colours and toughening the ceramic body.[5]

The influence of chemical composition on microstructure and mechanical properties of stoneware tiles has been studied by several workers.[5,8] Dondi et al.[5] found that the mechanical strength of tiles was improved by increasing the alumina content of the composition. Similarly, Harada et al.[9] also reported that additions of alumina to the feldspathic porcelain body could raise the flexural strength from

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80 to 150 MPa. Mukhopadhyay et al.[10] studied the effect of a talc addition on the thermo mechanical properties and microstructure of stoneware and found that the addition of 3% talc resulted in an increase in flexural strength and relative density, and a decrease in water absorption value.

There have also been numerous attempts to use alternative sources for the replacement of some of the raw materials used in commercial porcelainised stoneware body formulations. These include the utilisation of fly ash,[4] municipal incinerator grate slag,[6,7,11,12] soda-lime glass as a fluxing agent[13–15] and magnesium silicates,[16] zeolites,[17] wollastonite[18] in porcelainised stoneware bodies.

The aforementioned literature indicates that regardless of body compositions and raw material sources most of the studies carried out on porcelainised stoneware bodies are based on the conventional body which can be presented as a portion of the (Na_2O, K_2O)–Al_2O_3–SiO_2 ternary phase system and they favour mainly the growth of mullite ($3Al_2O_3{\cdot}2SiO_2$) crystals in the microstructure of fired product.

However, in this study an alternative porcelainised stoneware body composition has been formulated. In formulating the composition, it was aimed that the porcelainised stoneware should be composed mainly of anorthite ($CaO{\cdot}Al_2O_3{\cdot}2SiO_2$) crystals with glass present as a minor phase to effect densification.

Single firing porcelains[19–21] and whitewares[22] based on the formation of anorthite phase were also reported in the literature. For anorthite formation, wollastonite ($CaO{\cdot}SiO_2$) or similar minerals are added as a source of calcium oxide into kaolin, which is a source of alumina and silica.[23]

The aim of this study is to evaluate the possibility of using anorthite based material as porcelainised stoneware tiles. The behavioural properties and the microstructure of anorthite based material have been investigated using sintering study, flexural strength measurement, colorimeter techniques, X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques. Some technological and aesthetical results obtained on the anorthite-based material are compared to those of commercial porcelainised stoneware tiles.

2. Experimental

The starting materials used to make a particular anorthite-based composition, with a typical chemical analysis as given in Table 1, were FW 325 grade wollastonite, HTM-30 grade calcined alumina, SS-600 grade quartz, which were supplied by Doga Minerals, in Turkey and Ukranian Ball Clay, which was supplied by Kale Minerals, in Turkey. In previous studies,[22,24] it was found to be necessary to add magnesium to the starting materials to produce fired materials that would easily vitrify and become densified. It was added in the form of $(MgCO_3)_4{\cdot}Mg(OH)_2{\cdot}5H_2O$ and was supplied by Merck. The starting materials had the compositions or impurity contents shown in Table 2. The particle size distributions of starting materials are given in Fig. 1. The particle size distributions of the powders were analysed by a Coulter Multisizer AccuComp 1.19 model laser diffraction particle size analyser.

The technological behaviour of anorthite-based porcelainised stoneware materials was assessed by simulating, at

Table 1
Typical XRF analysis of the anorthite-based porcelainised stoneware body

Oxide	wt.%
SiO_2	42.54
Al_2O_3	37.73
CaO	11.26
TiO_2	0.21
Fe_2O_3	0.24
MgO	2.49
Na_2O	0.41
K_2O	0.40
L.O.I.	4.61

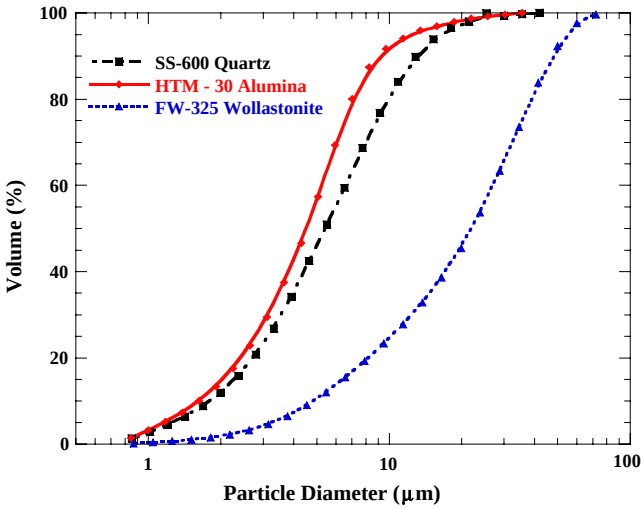

Fig. 1. Particle size distributions of raw materials.

Table 2
Chemical composition of raw materials

	Al_2O_3	SiO_2	CaO	MgO	Na_2O	K_2O	Fe_2O_3	TiO_2	L.O.I.
Wollastonite FW-325	1.0	52.0	43.2	1.0	0.2	0.2	0.25	–	1.2
Alumina HTM-30	99.5	0.020	–	–	0.3	–	0.020	0.007	0.12
Quartz SS-600	–	99.0	–	–	–	–	0.05	–	–
Ukranian Ball Clay	34.0	49.0	0.3	0.3	0.2	1.2	1.6	1.3	12.0
$4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$	–	–	≤0.75	40–45	–	–	≤0.002	–	–

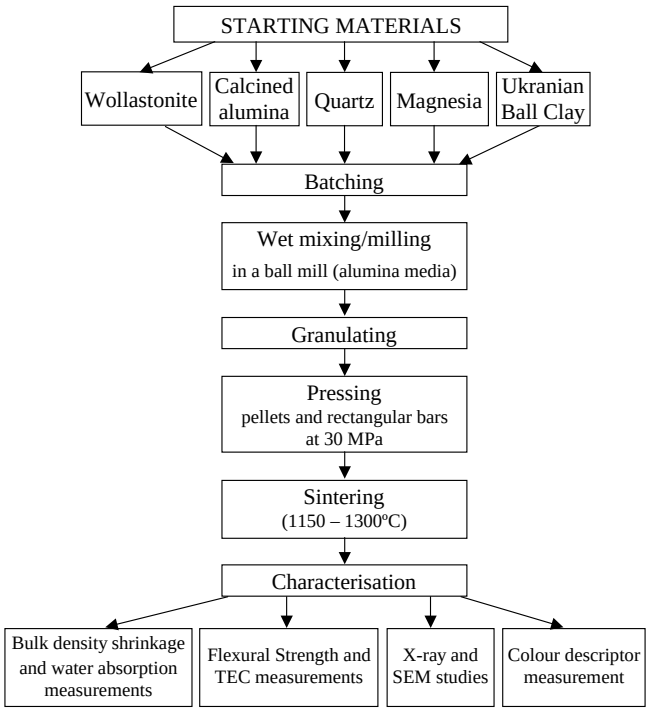

Fig. 2. Flow chart for the processing and characterisation of anorthite based porcelainised stoneware.

a laboratory scale, the stoneware making process (Fig. 2) and by characterising the finished products. In order to prepare 1 kg of batches appropriate amounts of starting materials were weighed and wet mixed/milled for 48 h in a 5 l porcelain pot containing 70 alumina balls ~15 mm in diameter. After mixing/milling, some slurry was withdrawn for particle size analysis and the remaining slurry was transferred to the plastic container and oven dried at ~110 °C. The powder cakes were broken up to form a powder, which was then granulated by first spraying with a fine mist of water droplets and then by agitating the damp powder. To produce the test samples, moist granules of the starting materials, were uniaxially pressed by means of a hand-operated hydraulic press at 30 MPa being maintained for 60 s. While the sintering study was carried out on disc test-pieces the flexural strength study was conducted on rectangular bars. The unfired bars had dimensions of 7 mm × 75 mm × ~4 mm. The unfired discs were 50 mm in diameter and ~3.5 mm thick. Both discs and rectangular bars were fired at temperatures from 1150 to 1300 °C with soaking times of 3 h, in the Nabertherm chamber kiln, to see how the materials densify.

The densities after firing were determined from the volume of discs and their masses. The firing shrinkages were determined by measuring the diameter of discs before and after sintering. The water absorption of the sintered discs was measured by a water displacement method. The flexural strength of sintered test bars were measured with an electronic universal tester (Model 5569, Instron Ltd.) by a three-point bending test with a lower span of 50 mm and crosshead speed of 1 mm/min, based on ASTM standard C1161-90. The surface condition of tested specimens was as-sintered. The number of samples used varied between 8 and 10 for each sintering temperature.

The crystalline phases present in the sintered samples were identified by XRD and SEM techniques. For XRD, powdered form of sintered samples were scanned from $2\Theta =$ 5 to 70°, at a scanning speed of 1°/min, using a RIGAKU 2000 DMAX diffractometer (with Cu Kα radiation, $\lambda =$ 0.154 nm) at 40 kV and 40 mA. The diffractometer was calibrated a silicon standard before use. The JCPDS cards listed in Fig. 7 were used to identify crystalline phases. For SEM observations, specimens were polished using 6, 3, and 1 μm diamond pastes after grinding with silicon carbide powders as abrasive and lubricated with water. The polished surfaces were chemically etched in 5% HF solution for 3 min. A Phillips XL30 SFEG scanning electron microscope equipped with EDAX detector (operating at 20 kV) was used for microstructural examination of samples with secondary electron images (SEI) used predominantly. Microanalysis was performed using the embedded EDX digital controller and control software.

The thermal expansion coefficient of a sintered specimen was determined between room temperature and 720 °C using a NETZSCH automatic dilatometer, at a heating rate of 10 K/min.

The whiteness and the colours of sintered discs were defined using the Minolta CR-300 colorimeter, in the reflection mode with a xenon light source. The colorimeter operates on the CIELab method, which is the most utilised technique in the ceramic industry to determine the whiteness and colour of the tiles by measuring the three parameters (Hunter parameters) L^* (brightness) from absolute white $L = 100$ to absolute black $L = 0$, a^* (red-green), b^* (yellow-blue) elaborated from the visible spectra.[25,26]

3. Results and discussion

Anorthite based body was processed and characterised. The results are compared with the results available in the literature for conventional porcelainised stoneware materials, in order to draw significant conclusion about the applicability of anorthite based material as a porcelainised stoneware.

It is widely recognised that the particle size distribution in a ceramic body has a significant impact on the packing efficiency, which in turn, influences the size and shape of pores, the shrinkage behaviour and microstructure development. The particle size analysis is performed and the results are given in Fig. 3. It can be seen that the analysis shows a bimodal distribution presenting two maximum points, which are centred at around 0.5 and 5 μm. The ratio between coarse and fine particle sizes is around 10, which is large enough for efficient particle packing.

Conventional porcelainised stonewares are typically fired in the temperature range from 1200 to 1230 °C to densify the body by the presence of glassy phase to obtain an open

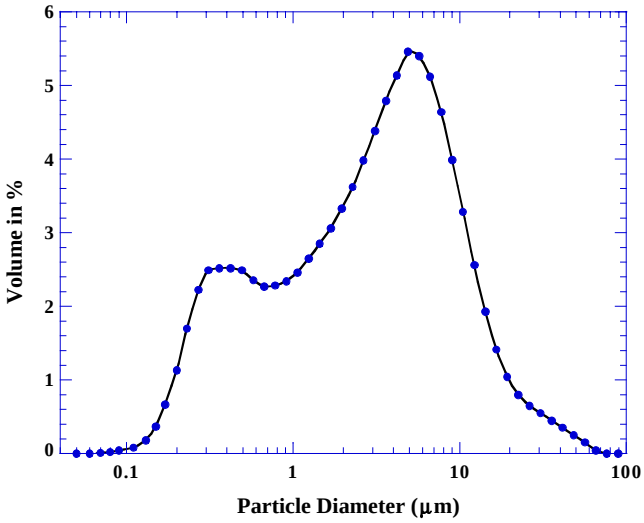

Fig. 3. The particle size distribution of anorthite based body mixture after 48 h mixing/milling.

porosity near to zero. Similarly, anorthite-based composition should be fired at a similar level of temperature.

To understand the densification behaviour, specimens of anorthite-based body were sintered in the temperature range from 1150 to 1300 °C with 25 °C intervals. The values of bulk density, firing shrinkage and water absorption were given in Figs. 4 and 5. As the sintering temperature increases, bulk density and firing shrinkage of the body continued to increase, reached a maximum at around 1200 °C, and then decreased. The decrease in density after reaching maximum is attributed to "*bloating*" (i.e., pore volume expansion), which arises from higher pressures (at high temperatures) of gases such as nitrogen, carbon monoxide and carbon dioxide entrapped within closed pores.

The formation of viscous liquid is the onset of vitrification and consequent densification. The vitrification temperature is defined as the temperature at which the apparent porosity becomes almost zero.

To investigate the extent of densification in the fired body, the apparent porosity, which is considered as the water absorption capacity of material is measured. Fig. 5 shows the variation in water absorption with sintering temperature. The ISO 13006 standard prescribes a maximum water absorption value of 0.5% for the porcelainised stoneware materials. As shown in Fig. 5, already at 1200 °C the water absorption of the sintered material becomes almost zero indicating that the fired body achieves of the standard's requirement.

The anorthite-based stoneware body densified well at 1200 °C, although the material was not significantly overfired to some 25 °C higher, as shown in Fig. 6. The finer pores appeared to have been removed from the material fired at 1200 °C and the material contains essentially isolated round pores in small numbers.

Fig. 5 shows the flexural strength behaviour of the body sintered in the temperature range from 1150 to 1275 °C. The flexural strength of the sintered material varied proportionally to its bulk density. The flexural strength of the material increased with an increase in sintering temperature up to 1200 °C. Upon further heating, the flexural strength reached a maximum and then decreased with a corresponding decrease in density. The fired strength also confirmed the maximum bulk density of the test specimens fired at 1225 °C.

Fig. 7 shows the X-ray diffraction patterns as a function of sintering temperature. The crystalline phases identified in all the specimens fired in the temperature range from 1150 to 1250 °C are anorthite being the major phase, cristobalite and corundum. While the peak intensity of anorthite increased significantly with the increase of sintering temperature, peak

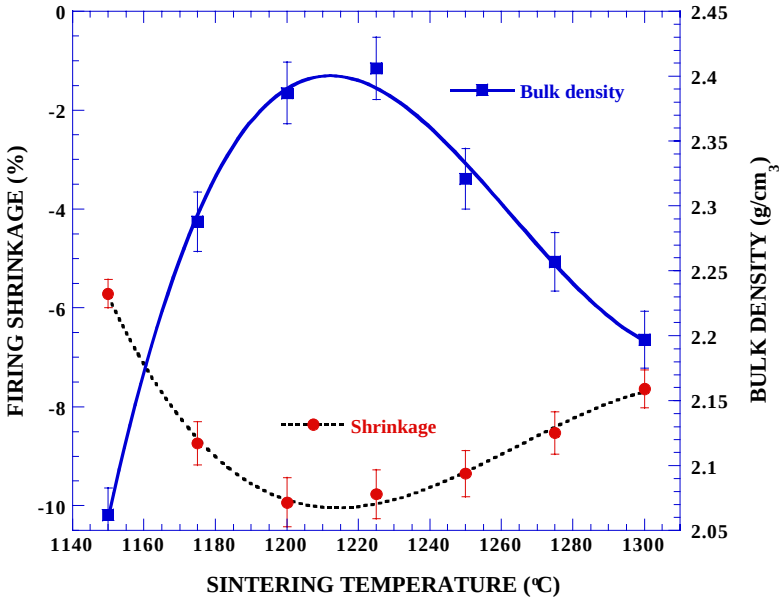

Fig. 4. Densification and shrinkage behaviour of anorthite based porcelainised stoneware.

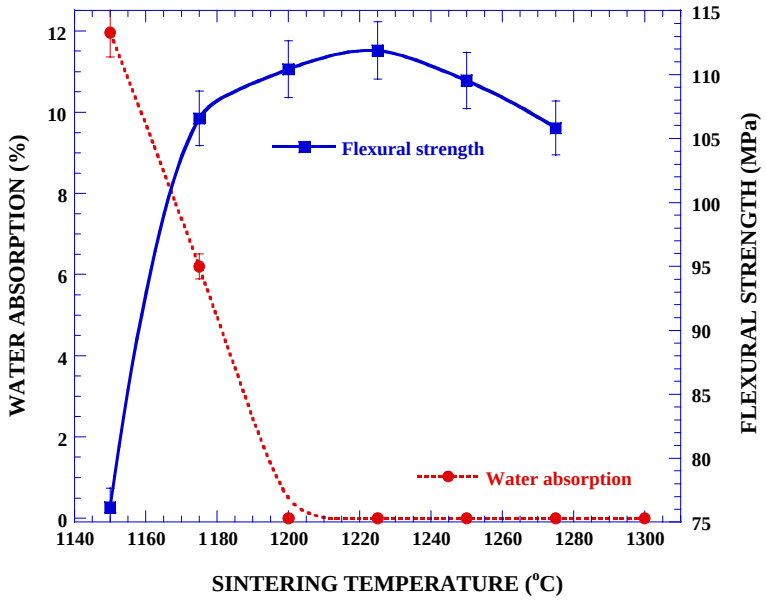

Fig. 5. Water absorption and flexural strength behaviour of anorthite based porcelainised stoneware.

heights for corundum and cristobalite decreased. This indicated that the increase of sintering temperature decreased the content of free cristobalite and corundum.

Quantitative X-ray analysis was carried out on the specimen fired at 1225 °C. It was found that this material contained ~52 wt.% anorthite, ~12 wt.% corundum and ~8 wt.% cristobalite with the remainder being glass. Contrary to the conventional materials, which contains about 65 wt.% glassy phase (~35 wt.% crystalline phase), anorthite based porselainised stoneware contains only ~28 wt.% (~72 wt.% crystalline phase).

SEM images given in Fig. 8a and b shows the highly crystalline microstructure of anorthite based porcelainised stoneware and typical anorthite grain, respectively. The EDX analysis in Fig. 8 indicates the formation of anorthite crystals, marked as A, corundum grains, marked as C, and cristobalite grains, marked as Q. Relatively small size corundum and cristoballite grains and glassy phase, marked as G, which is etched away to reveal the crystalline phases, are distributed between the anorthite grains.

The maximum flexural strength obtained with the anorthite based porcelainised stoneware is about 110 MPa which is much higher than that of commercial stoneware products (55 MPa). The bulk density of typical conventional porcelainised stonewares is in between 2.32 and 2.39 g/cm^3, their closed porosity ranges from approximately 7 to 12 vol.% and the size of porosities is varied between 1 and 50 μm.[5] The measured bulk density, calculated volume percent of

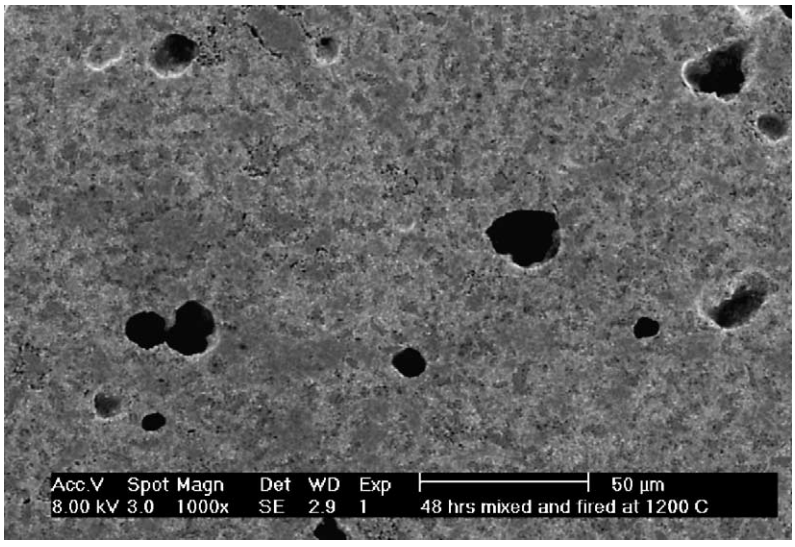

Fig. 6. The pore structure of anorthite based porselainized stoneware sintered at 1200 °C.

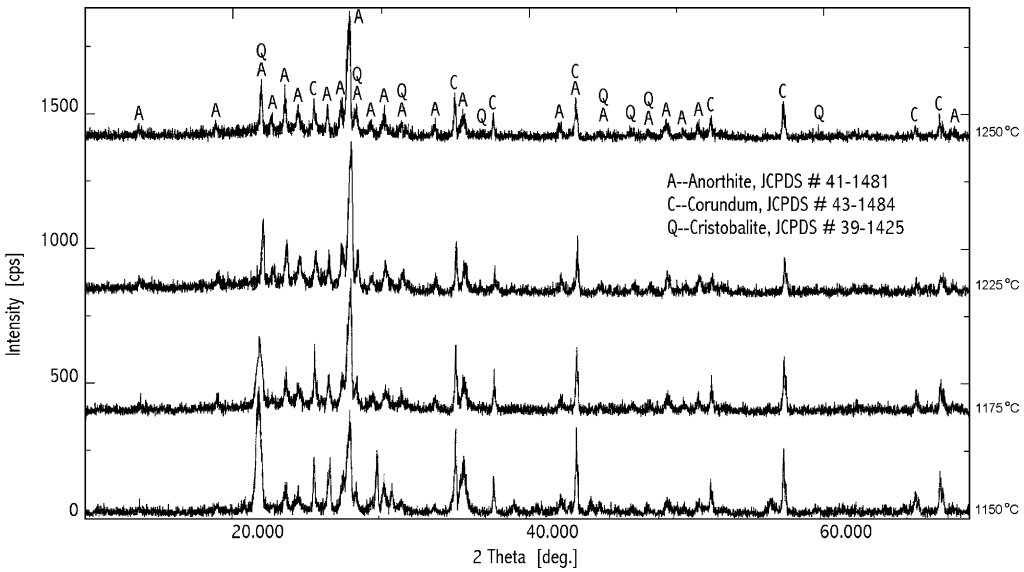

Fig. 7. XRD traces of anorthite based porcelainised stoneware body with sintering temperature showing anorthite, corundum and cristobalite formation labelled as A, C, Q, respectively.

closed porosity and the size of porosities of anorthite based porcelainised stoneware sintered at 1200 °C are 2.40 g/cm^3, 13 and 5 to 25 μm, respectively. Since the bulk density and amount of closed porosities of conventional and anorthite based porcelainised stoneware are almost the same, the high flexural strength of the anorthite based porcelainised stoneware could be due to either high crystalline to glass ratio or smaller porosity sizes or both.

The average thermal expansion coefficient (TEC) of anorthite based porcelainised stoneware over the temperature range 25 and 600 °C as shown in Fig. 9 was estimated to be ∼5.1 × 10^{-6} °C^{-1} which is much lower than the TEC value (∼7–9 × 10^{-6} °C^{-1}) of commercial products. This low TEC indicates that this material would be very resistant to being thermally shocked.

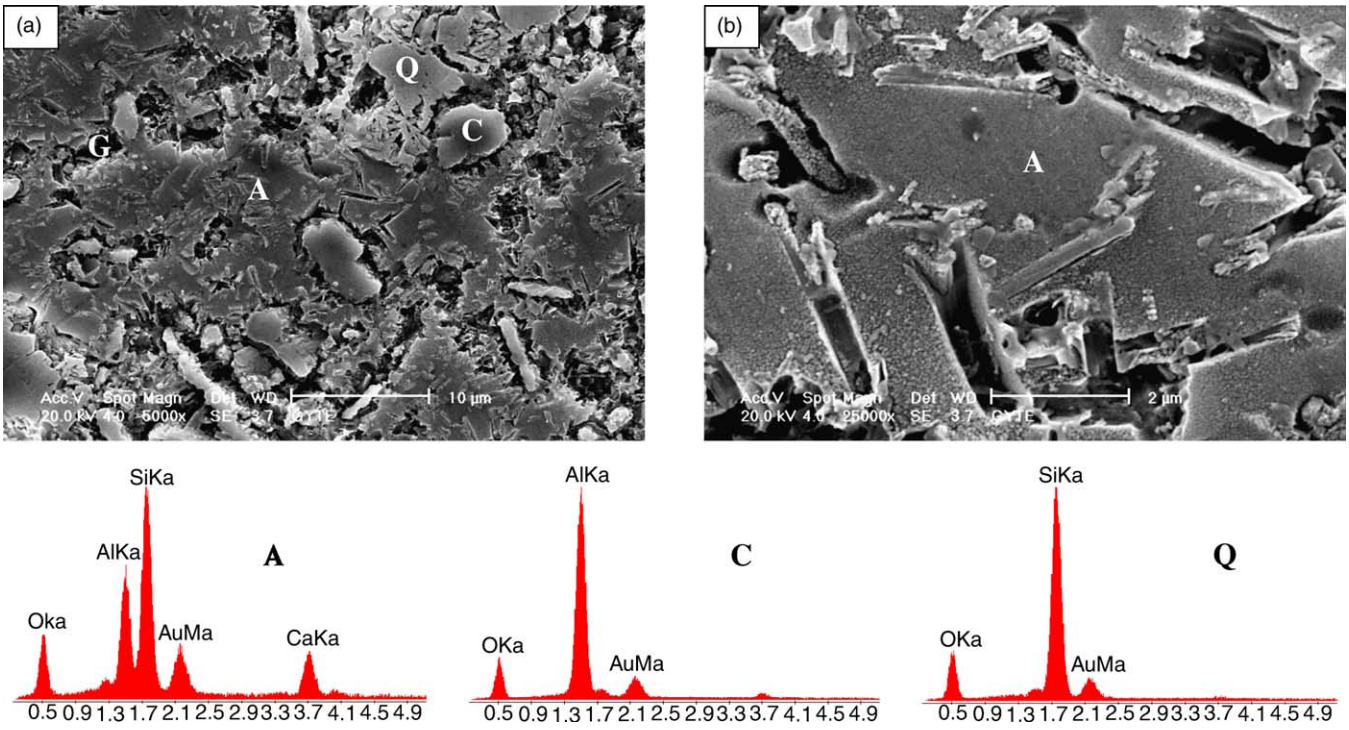

Fig. 8. The microstructure of anorthite based porcelainised stoneware at 1200 °C showing anorthite, corundum, cristobalite and glass formation labelled as A, C, Q, G, respectively. (a) Highly crystalline microstructure, (b) a typical anorthite grain.

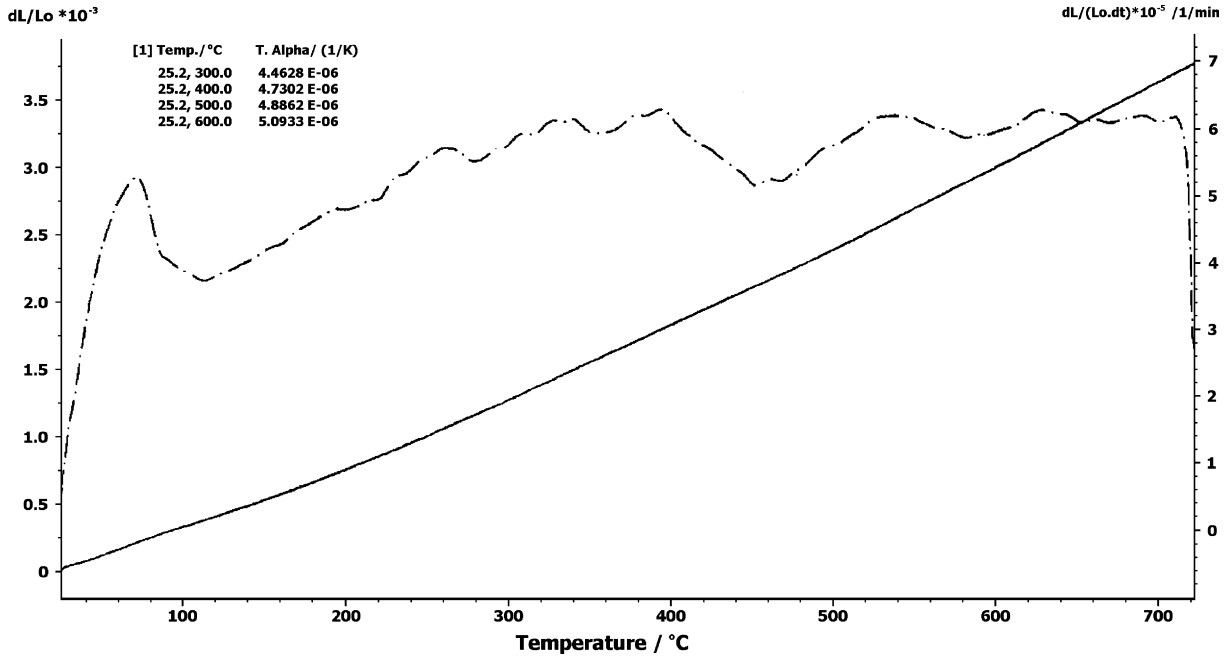

Fig. 9. Thermal expansion behaviour of anorthite based porcelainised stoneware.

The whiteness of the porcelainised stoneware is crucial for its marketing. To have some idea about the whiteness and to see how the whiteness is being affected with the sintering temperature the Hunter parameters of this new porcelanized stoneware material were measured and the results are shown in Fig. 10a and b. The colour difference values (a^*, b^*) of all the samples sintered at different temperatures are plotted together on the CIELab colour difference map in Fig. 10a, and the L^* parameters (whiteness) are plotted against the sintering temperature in Fig. 10b. It can be seen from Fig. 10a, that all the samples lie in the upper left quadrant with co-ordinates, in varying degrees, however, it appears evident that the variation of a^* and b^* Hunter parameters is not significant. A slight decrease in whiteness as a function of sintering temperature (Fig. 10b) is also observed, however, this again is not so marked. This slight variation in Hunter parameters could be due to a narrow range of sintering derived from the presence of a glassy phase formed that causes an increase of meltability. When the whiteness of the commercial products ($L^* = \sim 80$)[12] are taken into consideration the obtained values of L^* are quite remarkable. This new anorthite-based porcelainised stoneware material owes

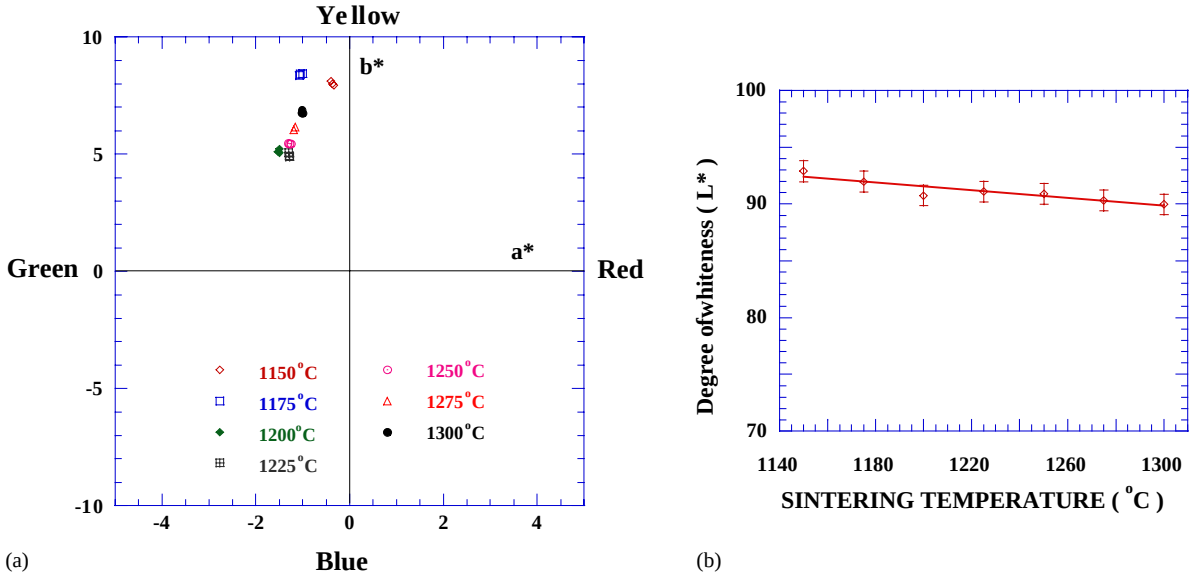

Fig. 10. (a) The colour difference map for anorthite based porcelainised stoneware. (b) Variation in degree of whiteness with sintering temperature.

its high degree of whiteness to the usage of raw materials containing low colouring impurities.

4. Conclusions

A new material from a mixture of wollastonite, alumina, quartz, magnesia and Ukranian Ball Clay has been designed and processed that enables all the porcelainised stoneware requirements to be met. It has been shown that it should be possible to densify this material in the 1200–1230 °C temperature ranges. The material has anorthite as its major phase (∼52 wt.%) with corundum (∼12 wt.%), cristobalite (∼8 wt.%) and glass (∼28 wt.%) as minor phases.

All the technological properties such as whiteness, water absorption thermal expansion coefficient and the flexural strength of the new material are significantly better than the properties of the conventional porcelainised stoneware. Without modifying substantially the process and technological conditions of the present industry the new material could be manufactured. Therefore, it is an excellent candidate material for stoneware industry.

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