DEVELOPMENT OF LOW TEMPERATURE PORCELAIN TILE BODIES WITH LOW-GRADE BORON BEARING MINERALS BY DRY ROUTE

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Low temperature sintered porcelain tile bodies can be obtained by formation of a low temperature liquid phase during viscous flow, and the subsequent enhancement of sintering mechanisms can be obtained with boron-containing minerals. This paper aims to develop an efficient utilization method for boron-containing minerals as fluxing agents in porcelain tile formulations in order to drastically reduce the peak firing temperature. Several batches of porcelain stoneware were formulated by replacing Na and Na-K feldspars used in manufacturing porcelain stoneware tile with different amounts of boron-containing minerals with a view to maximizing the addition. A dry granulation route was used in order to resolve the rheological problem of boron-bearing raw materials. A high amount of boron-bearing minerals induced remarkable changes in the type, amount and chemistry of the crystalline and amorphous phases of porcelain tiles. The crystallization and sintering behaviour of the porcelain body was investigated. The concurrent presence of alkaline and alkaline-earth elements with boron promoted the development of a low temperature viscous liquid phase, which improved the densification kinetics as long as it was operated within defined limits of the composition and firing regime. Further study is however needed on an industrial scale in order to establish the technical and economic feasibility of the study.

1. INTRODUCTION

Eti Mine Works is a Turkish state-owned mining and chemicals company focusing on boron products. It holds a government monopoly on the mining of borate minerals in Turkey, which possesses 72% of the world's known deposits. The main borate production areas are Bigadic, Emet and Kırka in Turkey [1].

Boron oxide-bearing minerals can be technologically considered as important alternative raw materials since they have a glass-forming character and have been used in the ceramic industry to reduce the melting point of the glassy phase [2] such as in the production of frits and glass. More recent studies have been carried out on the feasibility of decreasing the firing temperature of porcelain by using alternative fluxes. According to the relevant literature, there are various studies involving replacing potassium feldspar with soda-lime glass cullet [3], TV cathode ray tube or CRT glass [4], scrap alkali silicate glass [6], granite cutting sludge [6], glass ceramic frit [7]. The sintering temperature observed, lower (by around 100 °C) than feldspar based porcelain, makes it an economical alternative as well. Although the researchers have focused on their use in ceramic bodies destined for wet route processing, the use of borates in formulations of these bodies should be limited, in view of their partial solubility in water. However, a large group of water-soluble raw materials such as boron-bearing minerals also have a good potential to act as fluxing agents and could be used in dry route processes.

The main objective of the first part of this study is to obtain porcelain tile formulations by favouring crystallization with rapid firing at relatively low temperatures by using boron-containing minerals. Then, the second part of the study will focus on obtaining previously uninvestigated dense porcelain tile bodies by dry route from a combination of boron-containing minerals. In this paper, the aim is to study the feasibility of boron-containing natural minerals to act as alternative materials to partially replace the feldspar in porcelain stoneware bodies. In particular, in the paper, the results on the sintering behaviour of the composition studied are discussed.

2. MATERIALS AND METHOD

The boron-containing raw materials used in this study are ulexite (U2) and tincalconite (T1, T2 and T6) from the Eti Mine Boron Plant in Turkey (Bigadiç, Kırka region). The chemical analysis of the raw materials was carried out using a X-ray fluorescent (XRF) instrument. The chemical analysis of the boron-containing minerals was made by wet-chemical method. The chemical compositions of the raw materials used in the porcelain tile recipes are given in Table 1. Moreover, the mineralogical compositions of the selected boron-containing minerals are provided in Table 2.

	Clay	Na-Feldspar	Quartz	T-1	T-2	T-6	U-2
SiO_2	60.24	69.67	98.80	14.63	15.02	8.22	11.05
Al_2O_3	26.31	18.71	0.39	2.44	-	-	-
MgO	0.50	-	0.03	9.64	20.84	8.70	6.45
Fe_2O_3	1.21	0.14	0.05	0.46	0.15	0.27	-
K_2O	2.16	0.28	0.20	0.73	0.44	0.58	-
CaO	0.40	0.80	0.13	8.83	18.04	7.58	17,11
Na_2O	0.42	9.88	-	11.73	3.44	16.25	5.87
TiO_2	1.40	0.09	0.16	-	-	0.05	-
SO_3	-	-		0.12	0.29	0.30	0.20
B_2O_3	-	-		24.81	7.37	23.70	31.80
LOI.	7.21	0.53	0.12	26.49	34.41	30.04	27.52

***L.O.I.** Loss on ignition*

***Table 1.** Chemical compositions of the boron minerals and the raw materials (wt%)*

T-1	Tincalconite ($Na_2(B_4O_5\ (OH)_4)H_2O$), Sepiolite ($Mg_{7.68}(Si_{12}O_{30})(OH)_4(H_2O)_4(H_2O)_6$), Clinochlore ($Al_2Mg_5Si_3O_{10}\ (OH)_8$), Quartz ($SiO_2$), Pyrophyllite ($Al\ (Si_2O_5)(OH)$), Dolomite ($Ca\ Mg\ (CO_3)_2$), Probertite ($NaCaB_5O_7(OH)_4.3\ H_2O$)
T-2	Dolomite ($Ca\ Mg\ (CO_3)_2$), β- Disodium octoborate ($Na_2(B_8O_{13})$), Searlesite ($NaBSi_2O_5(OH)_2$), Magnesite ($MgCO_3$), Olshanskyite ($Ca_3B_4(OH)_{18}$)
T-6	Tincalconite ($Na_2(B_4O_5\ (OH)_4)H_2O$), Dolomite ($Ca\ Mg\ (CO_3)_2$), Sodium Borate (Na_3BO_3), δ- 2(SiO_2), Magnesite ($MgCO_3$)
U-2	Calcite Magnesium syn ($Mg_{0.03}Ca_{0.97}CO_3$), Calcium Sufite Sulfate Hydrate ($(Ca_3SO_3)\ 2SO_4\ (H_2O)$), Colemanite ($CaB_3O_4(OH)3H_2O$), Palygorskite-M ($Mg_5(Si_4O10)_2(OH)_2(H_2O)_8$), Ulexite ($NaCaB_5O_6(OH)_6\ (H_2O)_5$), Nobleite ($Ca\ B_6O_{10}\ 4\ H_2O$)

***Table 2.** Mineralogical composition of the boron-containing samples*

The use of boron-containing raw materials as a sintering aid in porcelain tile bodies, containing mixtures of clay, quartz and sodium feldspar, was investigated. In the first part of the study, porcelain tile compositions containing high amounts of boron were designed by optimizing the alkaline (Na_2O+K_2O), earth alkaline ($CaO+MgO$), B_2O_3 content and SiO_2/Al_2O_3 ratio in the composition. The formulations developed containing different types of boron minerals are given in Table 3 and the ternary diagram of the composition can be seen in Fig. 1.

Raw materials	R-8	R-9	R-16	R16-1	R-17	R-18	R19	R19-1
T-2	40	-	-	-	-	-	-	-
T-6	-	20	-	-	-	-	-	-
U2	-	-	15	15	20	25	-	-
T1	-	-	-	-	-	-	20	20
Clay	40	40	40	35	40	40	40	40
Quartz	10	20	25	10	20	20	20	20
Albite	10	20	20	40	20	15	20	20
Wollastonite	-	-	-	-	-	-	5	-
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Table 3. *Formulation of the experimental porcelain stoneware bodies (wt%)*

Oxides	R-8	R-9	R-16	R16-1	R17	R18	R-19	R19-1
Na_2O+K_2O	16	43	31.1	39.6	27.5	22	33.1	37.8
$CaO+MgO$	70.9	25.4	31.9	27.6	31.6	34.8	37.6	28.7
B_2O_3	13.1	31.6	37.0	32.2	40.9	43.2	29.3	33.5
Total	100	100	100	100	100	100	100	100
SiO_2/Al_2O_3								
Mole ratio	6.41	7.03	7.61	6.14	7.10	7.22	6.67	6.94
Oxide ratio	3.77	4.14	4.48	3.62	4.18	4.26	3.93	4.09

Table 4. *The glass phase composition (wt%)*

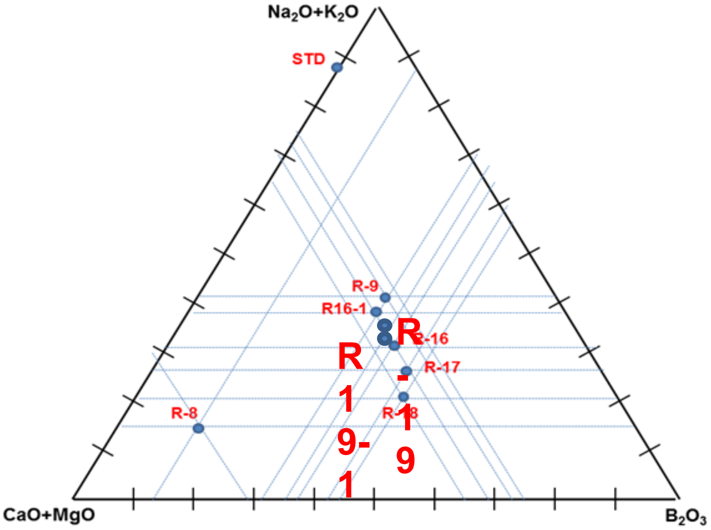

Fig. 1. *Ternary diagram of the studied composition*

All the formulations were tested at laboratory scale, simulating the industrial tile making process. The boron-containing raw materials were wet-ground in a jet mill with a low solids/water ratio high enough until the residue on 45 µm sieve was reduced down to 2-3%. The other components were also wet-ground in a jet mill until the same particle size was achieved and mixed. The slips obtained were allowed to dry in an oven at around 110 °C, then deagglomerated and humidified (5-6 wt% moisture content) and finally sieved down to 1 mm before pressing. Samples for sintering studies from each body formulation were prepared by dry pressing at a pressure of 400 kg/cm^2. They also were fired in a fast-firing laboratory furnace using a heating rate of 50 °C/min. with a dwell time of 5 min. The sintering behaviour was studied using a double beam optical non-contact dilatometer (MISURA ODHT-HSM 1600/80, Expert System Solutions, Italy).

Qualitative determination of the major crystalline phases was achieved by X-ray diffraction (Rigaku, Rint 2000, Japan). Microstructural observations were performed on fractured and etched surfaces of some selected fired samples using a scanning electron microscope (Zeiss Supratam 50 VP variable pressure FESEM). Qualitative EDX analyses were performed simultaneously with microstructural observations in order to distinguish the selected phases.

3. RESULTS AND DISCUSSION

The chemical composition of the raw materials is given in Table 1. The clay feldspar and the quartz present typical compositions used in the ceramic tile production. Boron-containing minerals (T1, T6 and U2) have a large amount of fluxing oxides (B_2O_3, Na_2O) and earth alkaline oxides such as MgO and CaO, which play an important role in the vitrification behaviour and ease liquid phase occurrence during sintering (Table 1). T2 is rich in CaO and MgO and pure in B_2O_3 compared with the other boron minerals. Chemical analysis revealed boron mineral T6, with a large amount of Na_2O and moderate fractions of CaO and MgO. In terms of mineralogy (Table 2) tincalconite ($Na_2B_4O_7.5H_2O$) and dolomite ($CaMg(CO_3)_2$) are the main phases in the case of T1, T6, with sodium borate, quartz, sepiolite present in minor quantities. For T2, the main phases identified were dolomite ($CaMg(CO_3)_2$), β-disodiuoctoborate ($Na_2(B_8O_{13})$), searlesite ($NaBSi_2O_5(OH)_2$), magnesite ($MgCO_3$), olshanskite ($Ca_3B_4(OH)_{18}$); as minor constituents. Boron does not occur in nature as a free element; instead, it occurs in nature as minerals associated with clay and other impurities. The T1, T2 and T6 used in the study are natural materials containing large amount of B_2O_3. These raw materials were selected due to their potential to act as fluxing agents during firing, as indicated by the chemical elements that make up their compositions, B_2O_3, Na_2O, CaO and MgO. The natural boron minerals selected offer economic advantages over boric acid and hydrated sodium borates but include complex mineralogical phases for which it is necessary to understand whether or not they contain materials suitable for porcelain tile production.

All the porcelain tile bodies studied, fired at different temperatures, were characterized through the determination of water absorption (ISO 10545-3) (Table 3). As is known, water absorption exhibits a decreasing trend with increased firing temperature. The water absorption capacity for ceramic bodies where less than 0.5% can be defined as porcelain ware. As seen from Table 3, the R-17 and R-18 formulations with high amounts of B_2O_3 in glassy phase compositions show higher water absorption with increasing peak temperature, most probably due to the bloating behaviour of the bodies before sintering. The optimum vitrifying range is achieved when apparent porosity attains a minimum value, which usually provides lower water absorption. On the other hand, firing above the optimum vitrifying temperature resulted in an adverse effect for water absorption because of an increase in the internal pressure inside the bodies. In these bodies (R17 and R18), which have high amounts of B_2O_3 in glass phase composition (Table 3), the sintering stops due to the bloating behaviour. The water absorption values of the R-16, R16-1, R-19 and R19-1 bodies studied are below 0.5% at a 1050-1100 °C temperature range. The fired samples are homogeneous and free of defects such as holes, bubbles or cracks.

Temperature (ºC)	**% Water absorption**							
	R-8	**R-9**	**R-16**	**R16-1**	**R-17**	**R-18**	**R-19**	**R19-1**
850	-	-	-	-	-	18.15		
900	-	-	-	-	5.32	29.31		
950	-	-	-	-	7.35	-		
1000	15.32	8.86	6.17	6.03	13.24	9.88	6.46	6.17
1050	-	-	1.60	0.2	-	-	2.35	0.42
1100	10.60	-	0.06	0.04	-	-	0.06	0.02

Table 4*. Water absorption values of the porcelain tile bodies studied*

The sintering behaviour of the bodies studied, containing varying amounts of boron-containing minerals (from 15 to 40 wt%) in partial replacement of Na-feldspar, is given in Figs. 2 and 3. The measurements were conducted using a continuous heating rate (25 °C/min.) up to 1050 °C to identify the sintering and bloating tendency of the samples. The sintering curves show the dimensional variations of the R-8 and R-9 samples subjected to the same thermal cycle (Fig. 2). R-8 and R-9 formulations including different type of boron minerals have completely different formulations and have an unusual sintering behaviour. For typical porcelain tile bodies, densification starts after 950 °C (i.e. in the melting range of sodium feldspar); in the range of 950-1220 °C total porosity decreases from 12 to 8% and, as a result, starts the transformation from open porosity into closed porosity; at 1200-1220 °C porosity becomes practically only closed with value of about 4.5%. Boron containing T2 addition on the composition of R-8 was highlighted by completely substituting the 30% Na-feldspar in standard porcelain tile compositions. The R-8 composition starts the sintering process at 750 °C, a lower temperature than traditional, and at 1050 °C open porosity is practically eliminated. The sintering curve is horizontal over a wide temperature range, between 800 °C and 950 °C; this means that the material does not undergo dimensional variations over an interval of more than 100 °C, most probably due to the formation of crystalline phases. Then shrinkage increases with a further increase in temperature and reaches maximum (3. 9%) at 1050 °C with 3 min. dwell time. The addition of T2 including large amounts of dolomite seems to cause a high amount of crystallization, most probably anorthite. The composition does not reach a stable dimension, indicating that it shows incomplete sintering due to the large amount of crystallization. The R-8 composition can be more suitable for wall tile products.

R-9 formulation including a higher amount of earth alkaline and B_2O_3 shows remarkably high sintering speed and does not reach a stable dimension over the temperature interval studied. The R-9 composition starts the sintering process at 720 °C, a lower temperature than traditional due to the Na_2O+B_2O_3 content as sintering promoters. The T6 boron mineral contains a high amount of Na_2O and moderate fractions of CaO and MgO, which come from dolomite. Decomposition of the dolomite causes the large amount of CO_2 gas to be generated at a relatively low temperature of 500-800 °C, which coincides with the beginning of the sintering. Because of the relatively low viscosity of the R-9 composition, particularly enriched in alkali (Na_2O) and B_2O_3, shrinkage starts at about 720 °C and reaches max. (1.3%) at about 980 °C. Then, however, due to the intensive formation of closed pores, densification stops. The occluded pores contain gas that exerts a pressure (*P*g) on the pore walls, acting against densification. At temperatures above 980 °C, occluded pore gas pressure is high and counteracts capillary pressure, causing the product to expand. Since the decomposition temperature is similar to the densification starting temperature of the porcelain green body (about 714 °C), the gas generated by thermal decomposition at the temperature (500–800 °C) in the green body is almost discharged before densification of the body and causes foaming during firing. The R-17 and R-18 compositions containing a large amount of boron also show the same sintering trend as in R9.

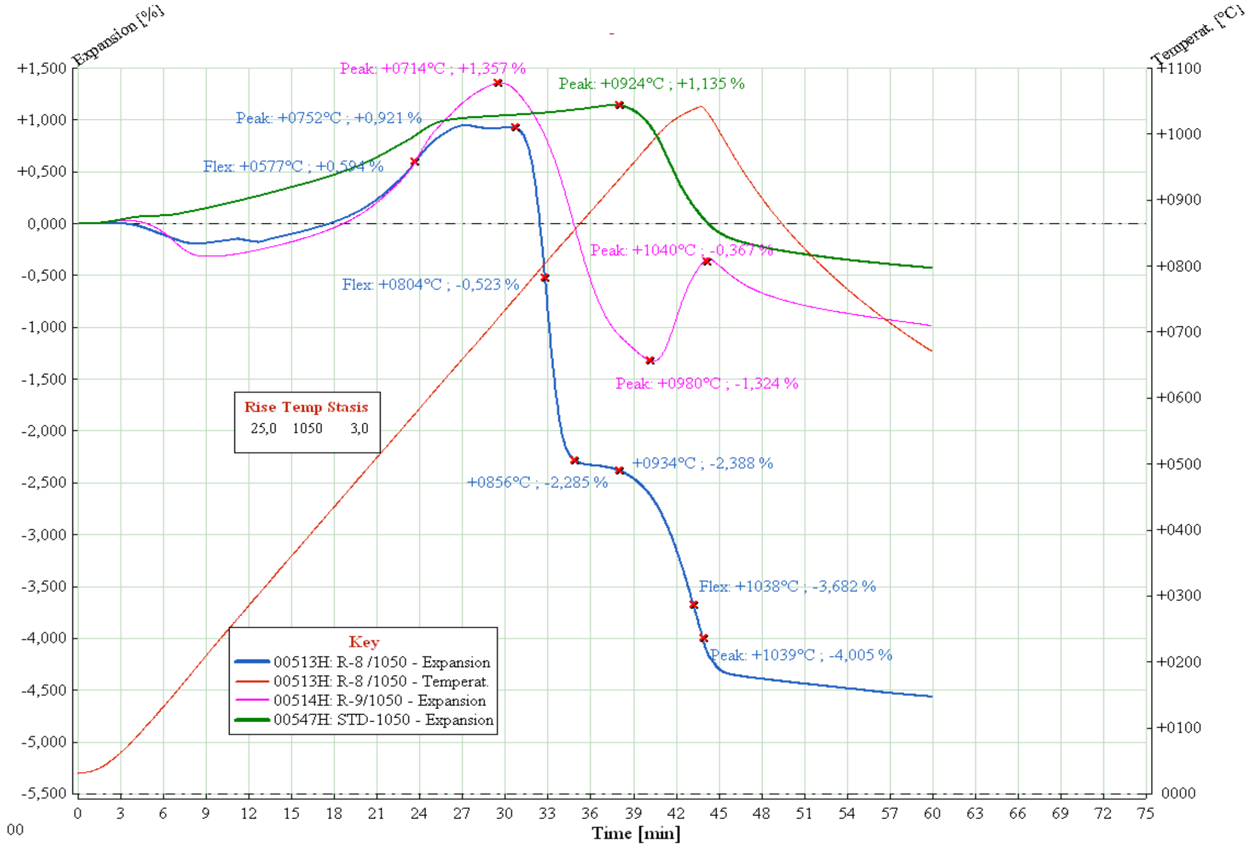

Fig. 2. *Sintering behaviour of the R-8 and R-9 compositions at 1050 °C with 3 min. dwell time*

The sintering behaviour of the formulations (R-16 and R16-1) containing 15 wt% U2 in partial replacement of Na-feldspar was given in Fig. 3. The R-16 and R16-1 compositions start the sintering process at ~720 °C. The two different flex temperatures corresponding to the maximum amount of shrinkage and maximum sintering speed were observed at 881 °C and 1031 °C for the R-16 composition. The first flex is due to the liquid phase derived from boron and partially melted feldspar, then there is a decreasing sintering speed due to the viscosity decrease. Considering the firing temperatures involved, crystallization of a calcium-rich phase, probably anorthite, took place. The liquid phase sintering proceeds after crystallization, and the second flex was seen at 1031 °C, which appears to be the optimum firing temperature for this particular composition. The R16-1 formulation also shows the same sintering behaviour with a higher sintering speed and shrinkage due to the higher amount of Na_2O in the glass phase (Table 3). The sintering behaviour of the formulations (R-19 and R19-1) containing 20 wt%. T1 in partial replacement of Na-feldspar is also given in Fig. 3. The two flex temperatures were observed at 835 °C and 1035 °C for the R19, but the sintering curve shifts to the higher temperature with decreasing shrinkage. According to the sintering curves, the maximum sintering temperatures increased with increasing amount of calcite. It is obvious that the refractoriness of the relevant formulations increases with increasing calcite content. The CaO reacts with the other oxides that are believed to cause the formation of an anorthite phase. Similar behaviour was observed for the R19-1 formulation, with higher sintering speed due to the lower CaO content in the composition. As seen from the sintering graph, with controlled combination of suitable raw materials, T1, T6 and U2, it is possible to achieve liquid phase formation at a lower temperature than in the case of feldspar. As expected, calcite content increased the refractoriness of the body due to the crystallization.

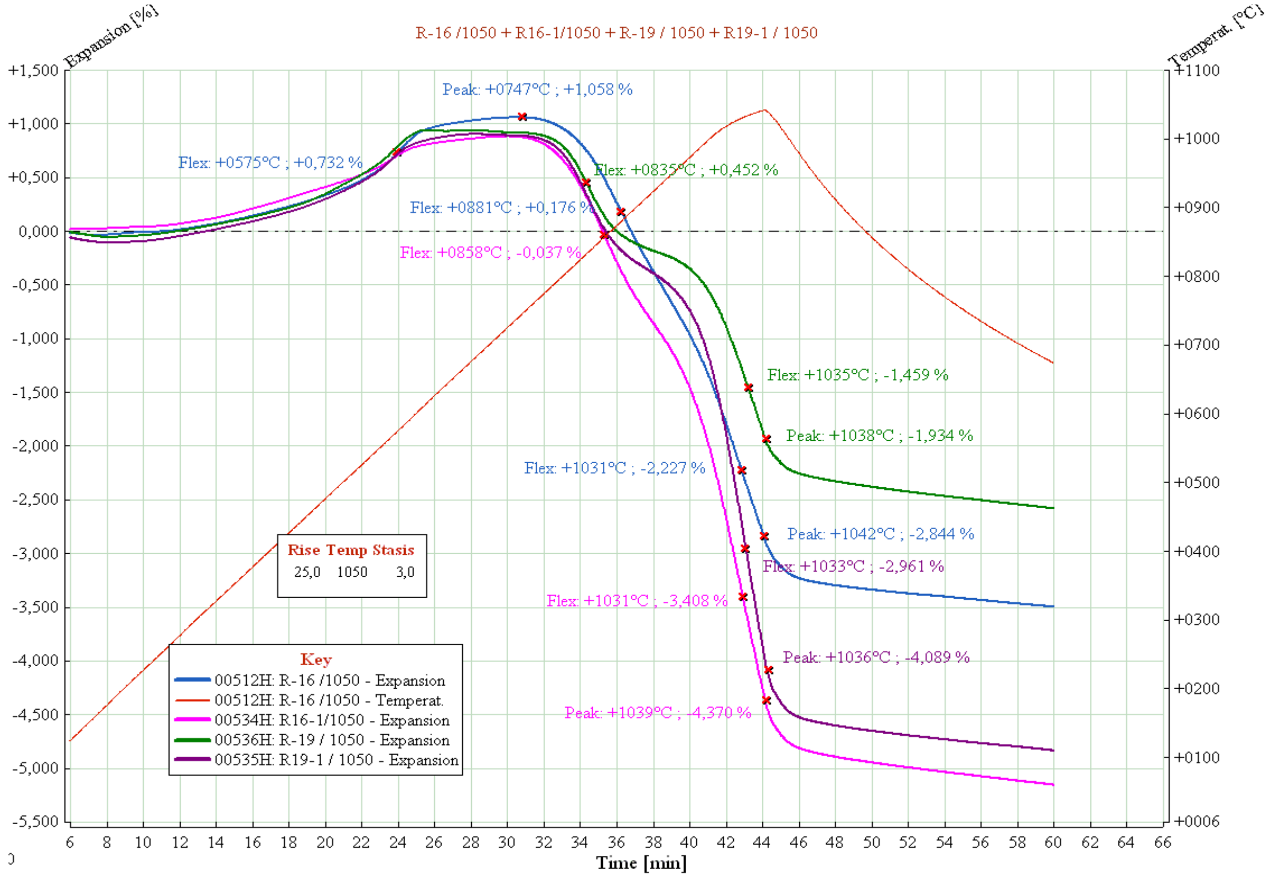

Fig. 3. *Sintering behaviour of R-16, R16-1, R-19, and R19-1 compositions at 1050 °C with 3 min. dwell time*

When boron minerals are exposed to heat, the mineral first loses crystalline water, followed by transformation of amorphous material or recrystallization into new phases [8]. The water molecules within the structure and its internal pressure increases rapidly which causes an explosive water loss with increasing temperature [9]. This sudden release within the micropores induces a disruption of the framework with increasing temperature [8, 9]. For this reason, direct use of boron mineral is limited as a raw material in ceramic industry. The other issue is that deformation problems will be observed in final products if boron-containing minerals are used at high amounts in ceramic products when they tend to densify in a fast firing process [10]. The heating rate, the most important parameter in decomposition of matter in shaped ceramic body, affects fast firing conditions. Conventionally, decomposition of boron minerals should be performed with very slow heating in order to avoid harmful effects of severe water release within micropores.

According to the XRD spectra of the selected fired formulations, namely R8, R9, R-16, R16-1, R-19 and R19-1 formulations, they contained residual quartz, albite and anorthite and abundant vitreous phase (Figs. 4 and 5). XRD data indicated the presence of anorthite as a new phase formed at low firing temperatures. This new phase is very probably anorthite sodian, with peaks very near to the ones of the residual albite, but the relative intensity is rather different. This result was also supported by the sintering test results obtained by optical dilatometer during industrial firing conditions. The temperature for the beginning of sintering decreases with increasing amounts of B_2O_3, and anorthite crystallization controls the sintering speed.

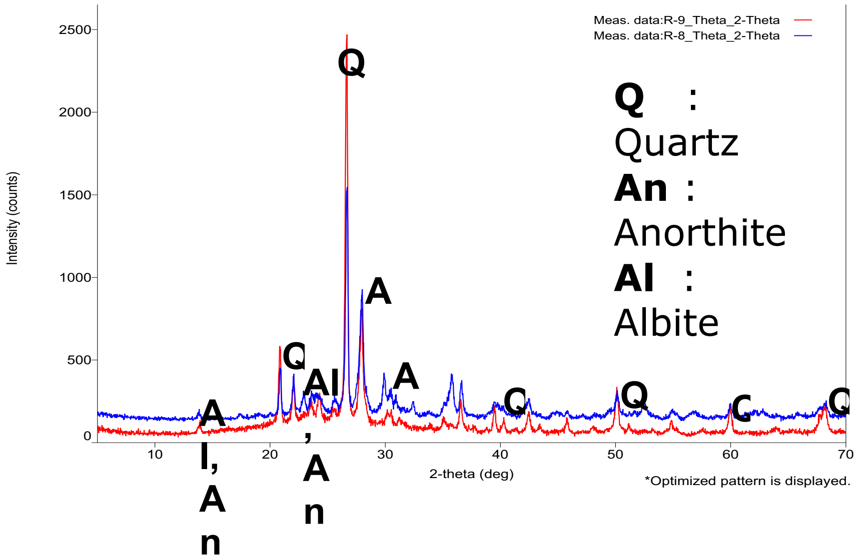

Fig. 4. *XRD spectra of the R-8 and R-9 bodies.*

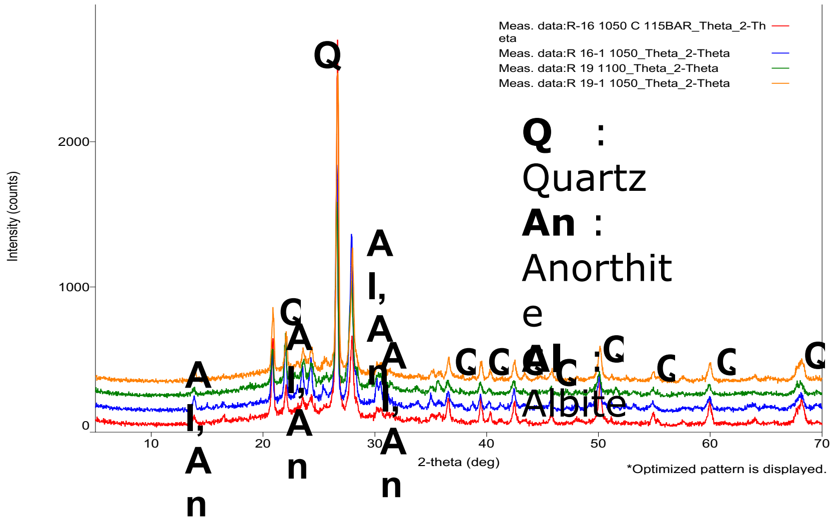

Fig. 5. *XRD spectra of R-16, R16-1, R19 and R19-1 bodies.*

Representative SEM images taken from the fractured surfaces of the formulation (R-16) fired at the optimum peak firing temperatures are presented in Fig. 5. The EDS analyses of the selected areas on the image are also given. The spheroidal crystal containing mainly elements of calcium, aluminium, silicon and oxygen shows the presence of a calcium-rich phase which is expected to be plagioclase (mixture of albite and anorthite). Considering the morphology of the crystals, anorthite is believed to be of primary formation.

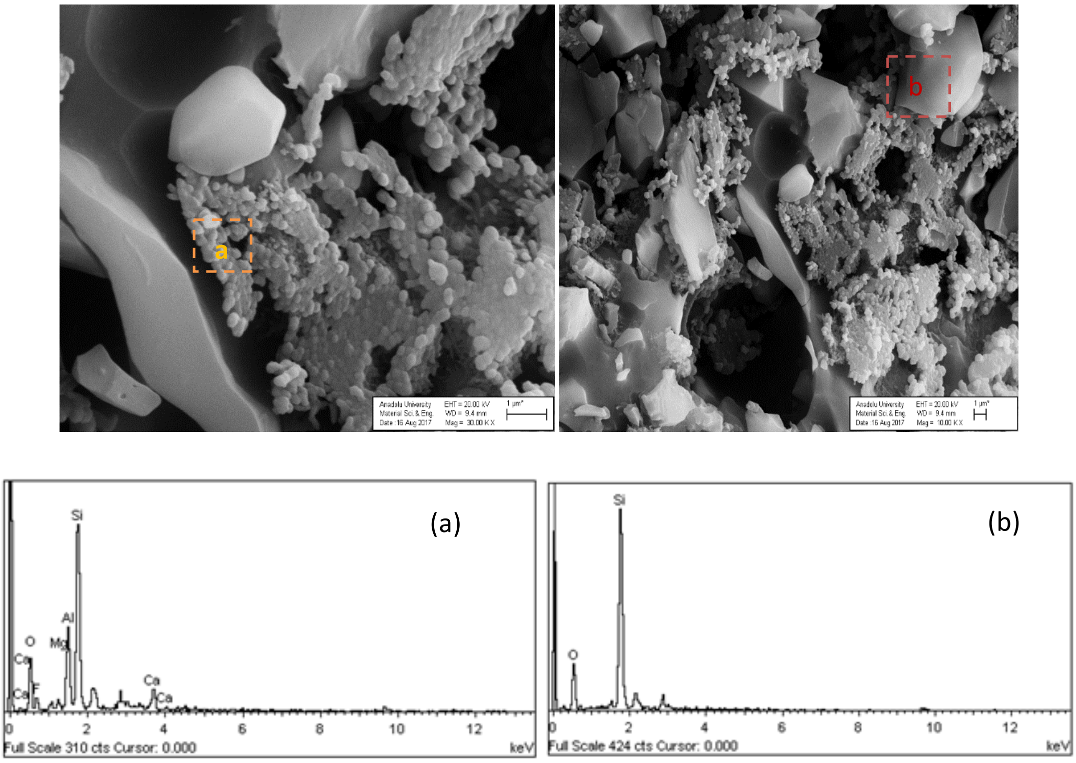

Fig. 11. *Typical SE images taken from the fractured, etched surfaces of R-16 formulation and the EDS analysis of areas shown in the figure.*

4. CONCLUSION

In this study, the possibility of replacing a percentage of the sodium feldspar with boron-containing minerals in a porcelain tile body was confirmed. The best results were obtained with the addition of U2 in the porcelain body formulations (R-16 and R16-1) due to its low melting behaviour with moderate anorthite crystallization and the greater homogeneity of the resulting bodies. The R-16 and R16-1 composition starts the sintering process at around 720 °C and sintering is completed at around 1000-1050 °C temperature range, which is about 150 to 200 °C lower than traditional. In addition, it was found that the CaO content in the formulations has a pronounced effect on the viscosity of the bodies. The viscosity increase due to the crystallization tendency plays a significant role in the sintering behaviour of the bodies studied. For the system studied, the critical oxide content of B_2O_3, CaO and Na_2O was noticed; 4-5 wt% for B_2O_3, 2.5 to 3.5 wt% CaO and 4-5 wt% Na_2O. Calcite content is one of the main factors determining the mineralogy of the sintered body and the extent of crystallization.

In relation to the foregoing role of feldspar in the porcelain body, boron-containing minerals as an alternative raw material can be suggested in small percentage (<20 wt%), whereas higher addition may cause deformation problems due to the high release of entrapped water molecules inside the boron minerals and decomposition products at higher temperatures. The conventional firing cycle should be performed with very slow heating at certain temperatures in order to avoid the harmful effect of the severe water release within micropores. Considering the mixture limitations of dry-route processes, an important point to keep in mind is the homogeneity of these fluxing agents in porcelain bodies, since their heterogeneity may preclude the use of these raw materials.

5. ACKNOWLEDGMENT

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