

Sintering behavior and properties of a talc-based cordierite composition with boron oxide additions

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Thermal reactions of impure raw materials of talc, alumina and kaolin were investigated to obtain cordierite ceramics by the addition of various amounts of boron oxide as sintering aid. Mixed powders were uniaxially pressed and sintered at temperatures varying from 900 to 1300 °C for 1 to 10 hours soaking time. The sintering behavior and the properties of sintered ceramics were examined by density, porosity and shrinkage measurements and also by XRD phase analysis and microstructural examination and analysis by SEM. Boron oxide additions to talc based-cordierite ceramics significantly affected the cordierite formation temperature and also the sintering behavior. The cordierite formation temperature was lowered by around 150 °C. These temperatures were 1050 °C for MT-3 and 1200 °C for MT-0 for 3 hours sintering time.

Key words: Cordierite, talc, kaolin, boron oxide, sintering, additives.

Introduction

Cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) is an important member in the ternary system $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$. It is characterized by a low thermal expansion and excellent thermal shock resistance. It also has a low dielectric constant. In view of these properties it is widely used as kiln furniture in the whiteware industry as well as in the micro-electronic packaging industry. It is also used as honeycomb monoliths coated with catalysts to combat automotive exhaust emissions to reduce pollution.

Normally, the conventional methods for the synthesis of cordierite ceramics include the solid-state sintering of individual oxides of magnesium, aluminium and silicon corresponding to the chemical composition of cordierite, crystallizing the glasses or the sintering of the natural raw materials having MgO , Al_2O_3 and SiO_2 contents, such as talc and china clay with a low silicon content.

Cordierite produced using the conventional solid-state reaction processing method is difficult to sinter at low temperatures without sintering aids due to its high sintering temperature [1]. Dense cordierite ceramics that could be fired below 1000 °C have been fabricated via some specialized methods such as sol-gel and crystallization of melt-derived glass [2, 3]. But in these methods the starting materials are expensive and the fabrication processes are complicated. The use of natural raw materials in cordierite production is favourable with their availability and prices. The difficulties of high temperature sintering can be overcome by the addition of sintering aids such as B_2O_3 ,

K_2O , Li_2O and La_2O_3 . Amongst the sintering aids, B_2O_3 has some advantages due to its low melting point and less harmful effect on the insulating characteristics than the other sintering aids. Although dense cordierite ceramics were obtained from ultrafine particles of $\text{Mg}(\text{OH})_2$ and kaolinite at 1350 °C [4], the addition of 3 wt% boron oxide into these mixtures promoted the densification at 850–900 °C [5].

The purpose of the present study was to produce cordierite ceramics from impure natural raw materials such as talc, kaolin and alumina. Also, the effect of boron oxide additions up to 3 wt% on the sintering behavior and properties of cordierite ceramics was studied and the results are discussed in view of the sintering behavior.

Experimental Procedures

The starting raw materials used were talc (from Eczacbaşı Essan of Turkey), kaolin (from Kalemaden of Turkey), alumina (A16 SG, Alcoa), and boric acid (from Eti Maden of Turkey). The chemical compositions of all the starting raw materials are given in Table 1.

MAS(2.2.5) is the stoichiometric composition of cordierite in the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system. B_2O_3 will be additional to 100 g of MAS compositions. The batch compositions

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

	MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3	TiO_2	Na_2O	K_2O	B_2O_3	LOI
Talc	34.4	0.78	62.1	1.36	0.36	-	-	-	-	1.0
Kaolin	-	36.92	47.80	0.31	0.62	0.31	0.01	0.73	-	13.3
Boric Acid	-	-	-	-	-	-	-	-	56.25	43.75
Alumina	-	100.00	-	-	-	-	-	-	-	-

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of the cordierite ceramics are given in Table 2, with added boric acid content. The position of the calculated composition of MT-0 is shown in Fig. 1 in the $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ phase diagram (6). It is seen that it lies in the cordierite phase region.

Batch preparation was carried out by ball-milling of the raw materials for 3 hours in porcelain jars with alumina balls. Drying of milled powders was done in an oven at 110°C .

Dry-pressing of all the samples were carried out by using uniaxial pressing in steel dies with a pressure of 1 ton/cm^2 (100 MPa). Rectangular bars were pressed for sintering studies. Sintering experiments were carried out in air for 1 to 10 hours with a heating rate of $5\text{ K}\cdot\text{minute}^{-1}$. Sintering temperatures were between $800\text{--}1300^\circ\text{C}$ with 50 and 100°C intervals.

The phase development of the as received and the sintered samples was studied by XRD (Shimadzu XRD-6000 diffractometer). The mechanical properties of the sintered samples were measured by applying the 3-point bending technique (Zwick/Z 1250 model Universal tester) at room temperature with a span of 25 mm and employing a cross head speed of $0.5\text{ mm}\cdot\text{minute}^{-1}$. An average of 5 measurements was evaluated as the strength value of the sintered samples.

Sintered densities and apparent porosities of the samples were measured applying the Archimedes principle in boiling water. Shrinkages in length and in thickness were measured from the dimensions.

Table 2. Batch compositions of MT cordierite ceramics

MT	Talc (gr)	Kaolin (gr)	Al_2O_3 (gr)	Boric acid (gr)
MT-0	469.76	317.73	112.31	0
MT-0.5	465.85	314.95	111.33	7.95
MT-1	461.61	312.08	110.32	16.00
MT-2	453.22	306.42	108.31	32.05
MT-3	444.94	300.82	106.33	47.99

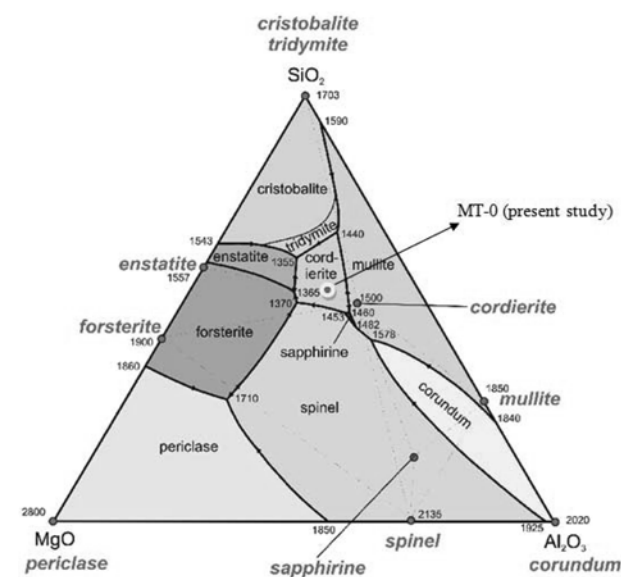
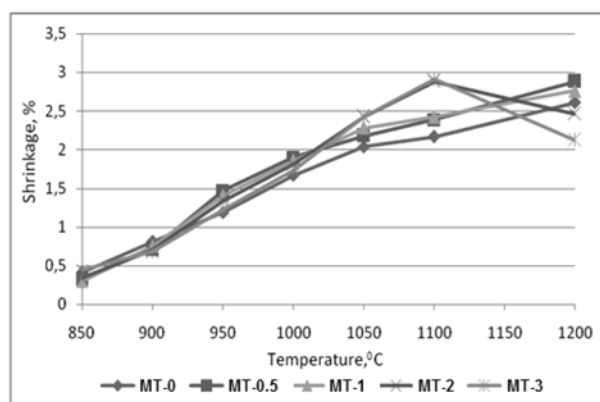


Fig. 1. $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ phase diagram (6).

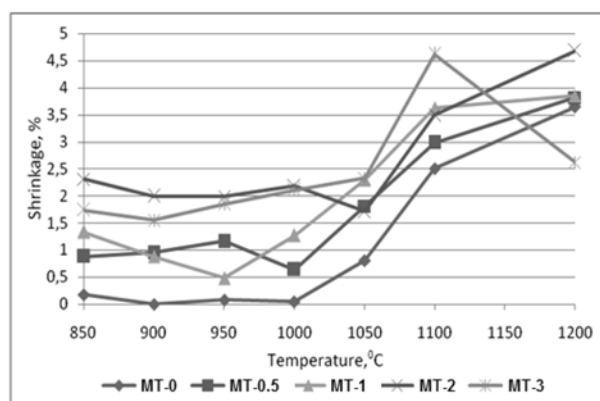
Thermal expansion coefficients of the sintered samples were measured by using a dilatometer (NETZSCH 402C/3/F) up to 1000°C in static air. Microstructural characterizations of the samples were carried out by using a scanning electron microscope (JEOL/SEM-6335F with INCA-EDS).

Results and Discussions

Fig. 2(a) and (b) show the shrinkage of the MT samples against sintering temperature with a sintering time of 3 hours. It can be seen that, the shrinkage values in thickness are higher than those of in length of the bar shape samples. At 1100°C , the shrinkage value in thickness is about 4.5% and that of in length is about 3%. The reason for this behavior is that, due to the kaolin, there is an alignment of the clay particles in dry-pressing perpendicular to the pressing directions as seen in Fig. 3. This alignment caused the differences in shrinkage in thickness and in length. A similar behaviors was also observed by Gunay [7] in spray-dried electrical porcelain granules. The alignment of clay particles, during the uniaxial pressing, affects the shrinkage behavior and the amount of shrinkage. The amount of shrinkage increased with an increase in the sintering temperature. Also, the amount of shrinkage increased with an increase in the B_2O_3 content and as expected the highest shrinkage values were in ceramics with 2 (MT-2) and 3 wt%



(a)



(b)

Fig. 2. Linear shrinkages of cordierite ceramics a) in length, b) in thickness with increasing sintering temperature.

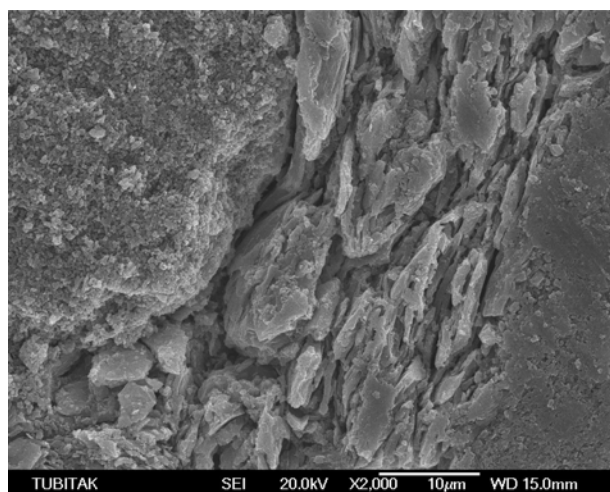


Fig. 3. Alignment of kaolin particles in MT-0 sample.

B_2O_3 (MT-3), additions at 1100 °C giving 2.8%. Above this temperatures there was a decrease in shrinkage in samples of MT-2 and MT-3 with 2 and 3% B_2O_3 additions. At 1200 °C with three hours sintering time, the shrinkage values in length were as ~2.6, ~2.8, ~2.7, ~2.5, and ~2.1% for MT-0, MT-0.5, MT-1, MT-2 and MT-3 respectively. A sharp decrease in the shrinkage values of MT-3 was also observed in thickness at 1200 °C. The shrinkage value for MT-3 was ~4.6% at 1100 °C and it was ~2.6% at 1200 °C, this can be due to the initiation of partial melting and bloating.

Fig. 4, shows the porosities of the MT samples with increasing sintering temperatures up to 1300 °C. Due to partial melting and bloating, no measurements were carried out for MT-2 and MT-3 at 1300 °C. The porosity values were around 19% for MT-0 and MT-0.5, and 17% for MT-1, 14% for MT-2 and 13% for MT-3 at 1200 °C for 3 hours. At 1300 °C, the lowest porosity was observed in MT-0.5 at 3% and the highest was in MT-0 at 13%. These results showed that the addition of small amount of B_2O_3 to MT system, increased the sintering behavior but high

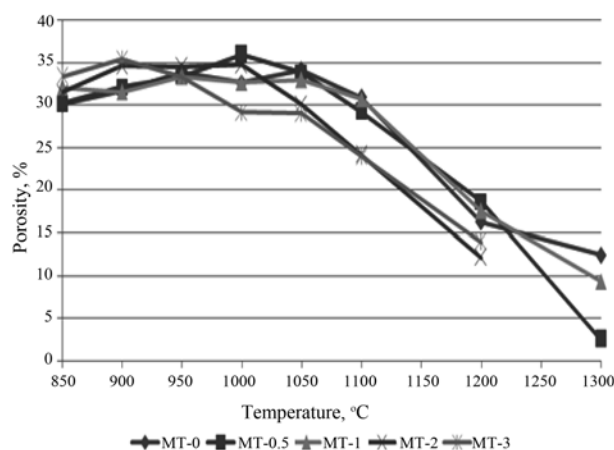


Fig. 4. Porosities of cordierite samples with increasing sintering temperature.

B_2O_3 contents were the reason for partial melting and bloating above 1200 °C.

Fig. 5, shows the effect of sintering time on the porosities in MT samples up to 10 h at 1100 °C. It is seen that, in all samples there was a small decrease in porosity with increasing sintering time, for example in MT-0 the porosity values were between 37 to ~25% for 1 h to 10 h, respectively. In MT-3, the values were between 25 to 17% for 1 h and 10 h, respectively. These results showed the possibility of reducing or controlling the amount of porosities in MT ceramics at a lower temperature by changing the sintering time.

In Fig. 6, the changes in density with increasing sintering temperature is shown. The highest density value was in MT-0.5 as 2.42 g/cm³ and it was 2.22 g/cm³ for MT-0 at 1300 °C for 3 hours. At this temperature, the density value of MT-1 was around 2.12 g/cm³. This can be due to the partial melting and bloating. At 1200 °C for 3 h, all the MT samples had density values of around 2.2 g/cm³ and these values were around 2.0 g/cm³ at 1100 °C after 3 h sintering time. The effect of sintering time at 1100 °C is shown in Fig. 7 and it is seen that the effect of sintering time was not considerable.

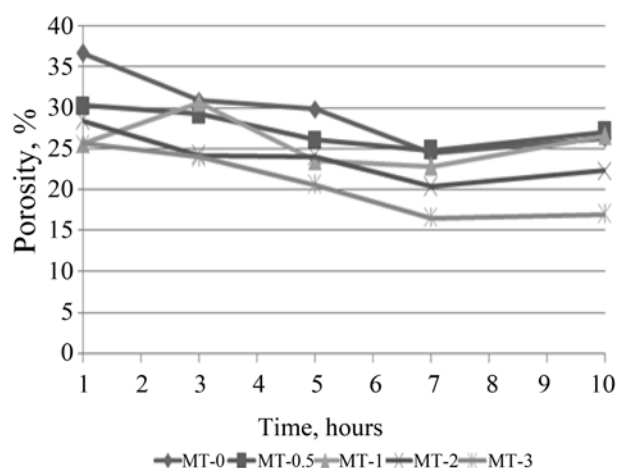


Fig. 5. Porosities of cordierite samples with increasing sintering time at 1100 °C.

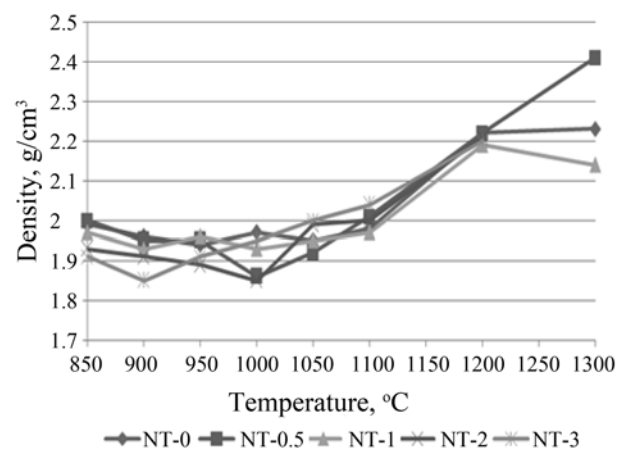


Fig. 6. Densities in cordierite ceramics with increasing sintering temperature.

The mechanical behavior of all the MT samples are shown in Fig. 8 with increasing sintering temperature. Up to 1100 °C for 3 h, the flexural strength values were low and show small increases. The flexural strength values were ~8 MPa for MT-0 and 20 MPa for MT-3 at 1000 °C. Above 1100 °C, there were sharp increases for MT-0, MT-0.5 and MT-1 but there were nearly no increases in flexural strength of MT-2 and MT-3 up to 1200 °C. Due to the partial melting no flexural strength measurements were carried out for MT-2 and MT-3. At 1200 °C, the flexural strength values were, 68 MPa for MT-0, ~40 MPa for MT-0.5, 30 MPa for MT-1, 20 MPa for MT-2 and 10 MPa for MT-3. This behavior is shown in Fig. 9, where the addition of B₂O₃ is seen as useful in flexural strength values at lower sintering temperatures for example at 1000 °C. It is seen that, the flexural strength values increased with increasing B₂O₃ content. At 1300 °C for 3 h, the flexural strength value of MT-0 was nearly the same as the

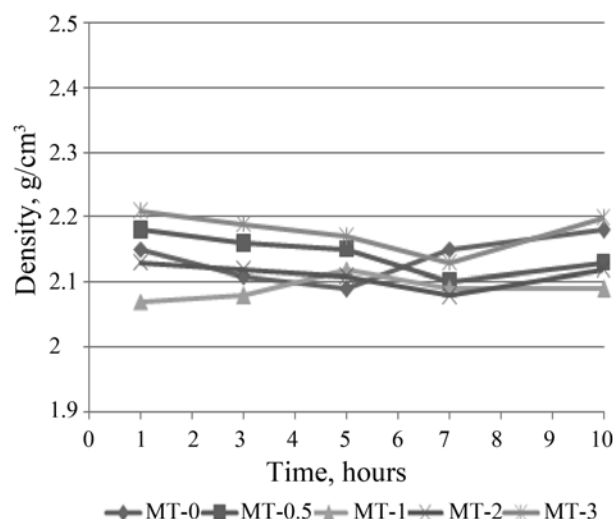


Fig. 7. Densities of cordierite samples with increasing sintering time at 1100 °C.

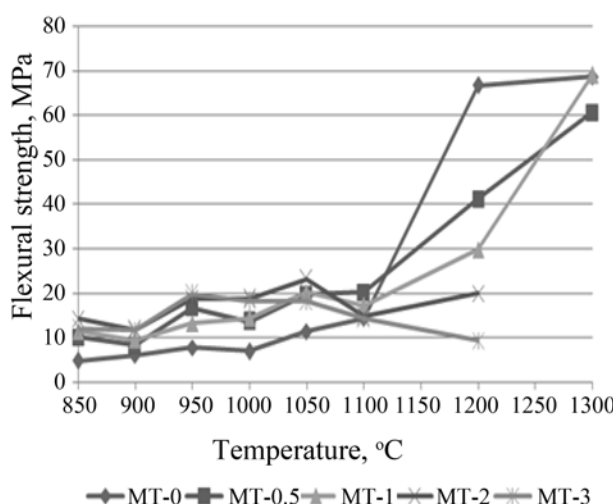


Fig. 8. Flexural strength values of cordierite ceramics with increasing sintering temperature.

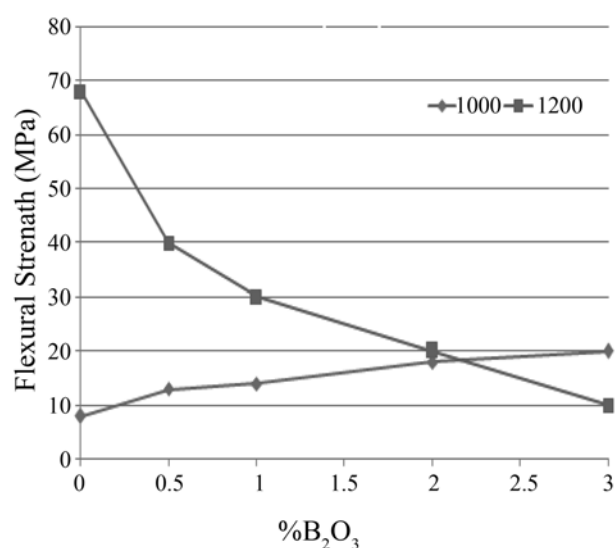


Fig. 9. Flexural strength of cordierite ceramics with increasing B₂O₃ content at 1000 and 1200 °C for 3 hours.

value at 1200 °C, but the flexural strength value of MT-0.5 was around 60 MPa and the flexural strength value of MT-1 was similar to MT-0 at around 68 MPa. As a result, small additions of B₂O₃ (up to 1%) to the MT system are effective at higher sintering temperatures but high B₂O₃ additions were not effective above 1100 °C in improving the flexural strength.

XRD analysis showed that MT cordierite ceramics contain several phases; corundum (Al₂O₃), enstatite (MgO·SiO₂), quartz (SiO₂), cristobalite (SiO₂), cordierite (2MgO·2Al₂O₃·5SiO₂), mullite (2Al₂O₃·3SiO₂) and fosterite (2MgO·SiO₂) as crystalline phases. The crystalline phases are given in Table 3(a), with increasing sintering temperature for 3 h sintering time up to 1300 °C. The talc phase disappeared at 950 °C and up to 1050 °C, corundum, enstatite and quartz were the phases present in the MT samples. The first cordierite phase was observed at 1050 °C in the sample of MT-3 (with 3% B₂O₃ addition). At 1100 °C, cordierite phase appeared in all the samples with a B₂O₃ content except for the sample MT-0 which had no B₂O₃. In this sample, the cordierite phase was observed at 1200 °C. These results showed that, the addition of B₂O₃ to the MT system affected the formation of the cordierite phase by lowering the cordierite formation to 1050 °C instead of around 1200 °C.

The crystalline phases in the MT system are also given in Table 3(b), with increasing sintering time from 1 h to 10 h at 1100 °C. As can be seen, Cordierite appeared after 7 h sintering time in MT-0. This result also showed that the sintering time affected the cordierite phase formation. The important detail in phase development is that the addition of B₂O₃ in cordierite ceramics influences the formation of the cordierite phase and reduces the cordierite formation temperature to 1050 °C compared to around 1200 °C in the sample without a B₂O₃ content.

These phases are also effected the thermal expansion behavior of the samples and Fig. 10, shows the changes

Table 3(a). Phase identification of cordierite samples with increasing sintering temperature for 3 hours sintering time

	850 °C	900 °C	950 °C	1000 °C	1050 °C	1100 °C	1200 °C	1300 °C
MT-0	T+C+Q+E	T+C+Q+E	C+Q+E	C+E+Q	C+E+Q	E+C+M+Q+Cr	Cor+Cr+C+E+M	Cor+E+C+M+Cr
MT-0.5	T+C+Q+E	T+C+Q+E	C+Q+E	C+E+Q	C+E+Q+M+Cr	Cr+E+C+Q+M+Cor	Cr+Cor+E+C+M	Cor+E+C+M+Cr
MT-1	T+C+Q+E	T+C+Q+E	C+Q+E	C+E+Q	C+E+Q+Cr+M	Cr+C+E+Q+M+Cor	Cr+Cor+E+C+M	Cor+E+C+M+Cr
MT-2	T+C+Q+E	T+C+Q+E	C+Q+E	C+E+Q	Cr+C+E+Q+M	Cr+C+E+Cor+M	Cor+Cr+E+C+M	MELT
MT-3	T+C+Q+E	T+C+Q+E	C+Q+E	C+E+Q	Cr+C+E+Q+M+Cor	Cr+C+Cor+E+M	Cr+Cor+C+M+E	MELT

C : corundum, E : enstatite, Q : quartz, Cr : Cristobalite, F : forsterite, Cor : cordierite, M : mullite

Table 3(b). Phase identification of cordierite samples with increasing sintering times at 1100 °C

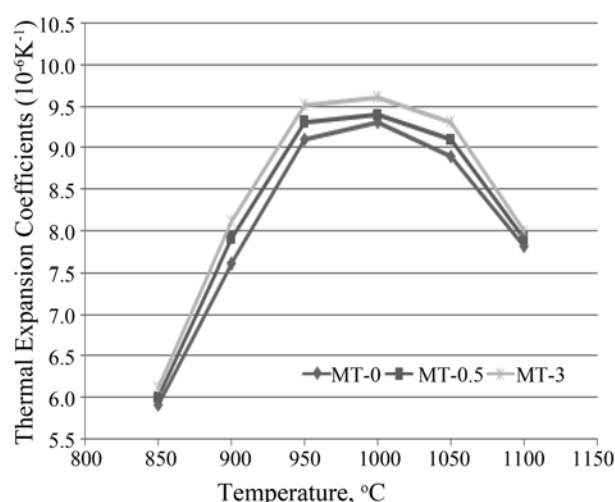
	1 h	3 h	5 h	7 h	10 h
MT-0	E+C+M+Q+Cr	E+Cr+C+M+Q	Cr+E+C+M+Q+Cor	Cr+E+C+M+Q+Cor	Cor+Cr+C+E+M
MT-0.5	Cr+C+E+M+Cor+Q	Cr+C+E+Cor+M+Q	Cr+C+E+Cor+M	Cr+C+E+Cor+M	Cr+Cor+E+C+M
MT-1	Cr+C+E+Cor+M+Q	Cr+C+Cor+E+M+Q	Cr+C+E+Cor+M	Cr+C+E+Cor+M	Cr+Cor+E+C+M
MT-2	Cr+C+E+Cor+M	Cr+C+Cor+E+M	Cr+Cor+C+E+M	Cr+Cor+C+M+E	Cor+Cr+E+C+M
MT-3	Cr+C+E+Cor+M	Cr+C+Cor+E+M	Cr+Cor+C+E+M	Cor+Cr+E+M+C	Cr+Cor+C+M+E

C : corundum, E : enstatite, Q : quartz, Cr : Cristobalite, F : forsterite , Cor:cordierite, M : mullite

in TEC (thermal expansion coefficient) value of samples sintered at various temperatures for 3 hours. The highest TEC values were in MT-0.5 over $9.5 \times 10^{-6} \text{ K}^{-1}$ at 1000 °C and the other samples with various B_2O_3 contents, had similar TEC values around $8.5 \times 10^{-6} \text{ K}^{-1}$. At lower sintering temperatures such as at 850 °C the TEC values for all the samples were around $6 \times 10^{-6} \text{ K}^{-1}$, also at higher sintering temperatures such as at 1100 °C the TEC values for MT-0 and MT-3 were just over $7.5 \times 10^{-6} \text{ K}^{-1}$. This drop of the TEC values was due to the formation of the cordierite phase in the ceramics. These TEC values are quite high for cordierite ceramics but as seen in the XRD results there are several phases in the MT ceramics and in particular cristobalite has large effect on TEC values in the system because of its high TEC value of around $10 \times 10^{-6} \text{ K}^{-1}$

[8, 9]. It is well known that, cristobalite increases the TEC values of ceramic systems and it was reported by Kobayashi *et al* [10] that cristobalite formation is very effective on the TEC values of $\alpha\text{-Al}_2\text{O}_3$ reinforced porcelain bodies and around a 30–40% quartz addition to the body resulted in TEC values of around $7.5 \times 10^{-6} \text{ K}^{-1}$. In the present study, the total amount of cristobalite and quartz phases ($\text{TEC} \sim 14 \times 10^{-6} \text{ K}^{-1}$) was around 22% and the amount of corundum was around 38% after sintering at 1000 °C. Also, corundum ($\alpha\text{-Al}_2\text{O}_3$) phase has large TEC values ($8.8 \times 10^{-6} \text{ K}^{-1}$) in the system. The high TEC values in MT ceramics can be justified by considering the large amount of cristobalite and corundum phases present.

Microstructural investigations by SEM also revealed that, there are multiple phases in MT cordierite ceramics. The SEM-EDX technique was applied to the analysis of different regions in samples and as shown in Fig. 11, there are some regions (spectrum 1) where only alumina was detected, and in some regions (spectrum 2) reacted phases containing Mg, Al, Si, were detected. The more detailed microstructure of the alumina region is given in Fig. 12, where it is seen that there are very fine alumina particles with a particle size which usually sub-micrometre. These alumina particles are the product of dissolving kaolin during sintering to cristobalite and alumina, at higher temperatures mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) formation started but at a lower temperatures kaolin dissolved to form Al_2O_3 and SiO_2 as corundum and cristobalite. The cordierite regions are the most reacted regions and talc reacts with kaolin and alumina to form cordierite. During these reactions, cristobalite is formed due to the dissociation of kaolin to cristobalite and alumina, otherwise there should not be any cristobalite in the system but the XRD results revealed that there was a high content of cristobalite phases in MT

**Fig. 10.** Changes in TEC of cordierite ceramics with increasing sintering temperature.

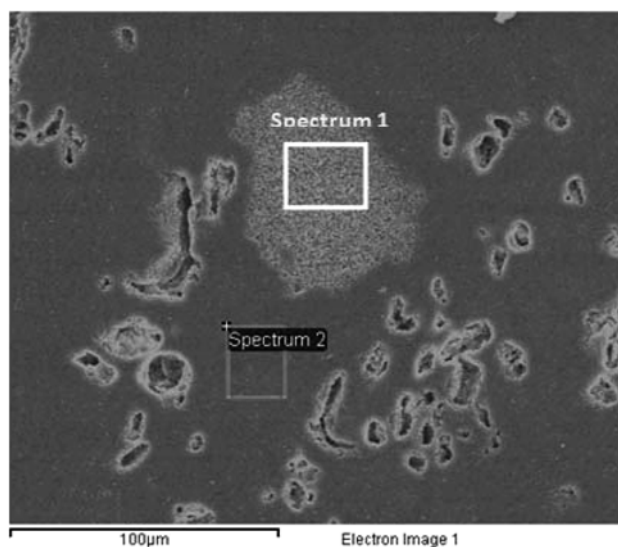


Fig. 11. A SEM micrograph of two different phase regions in MT-0 at 1200 °C with their compositions.

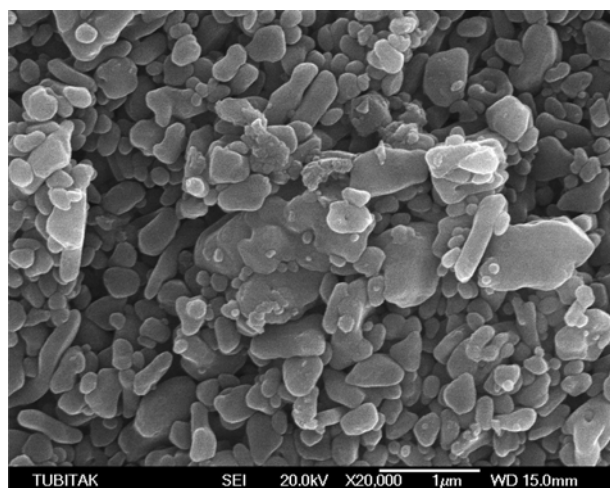


Fig. 12. Alumina region in cordierite ceramic.

cordierite ceramics. Kaolinite is an atomically layered structure of $(\text{Si}_2\text{O}_5)^{2-}$ and $(\text{Al}_2(\text{OH})_4)^{2+}$ molecular sheets, but the level of mixing of Si and Al is not sufficient to prevent the segregation of alumina and amorphous silica which crystallizes as α -cristobalite at high temperatures [11]. This behavior and detailed phase development in this system will be the subject of another publication.

In Fig. 13, the beginning of partial melting is shown in MT-3 at 1200 °C for 3 hours. Also, it can be seen that the bloating had just started and some large pores are visible in the microstructure. In the MT-3 sample with 3% B_2O_3 addition, after sintering at 1200 °C, the partial melting and bloating extended and the samples were bloated. Due to this, no measurements were carried out on these samples.

Conclusions

The use of natural raw materials in the preparation of cordierite ceramics is very important in an economical sense

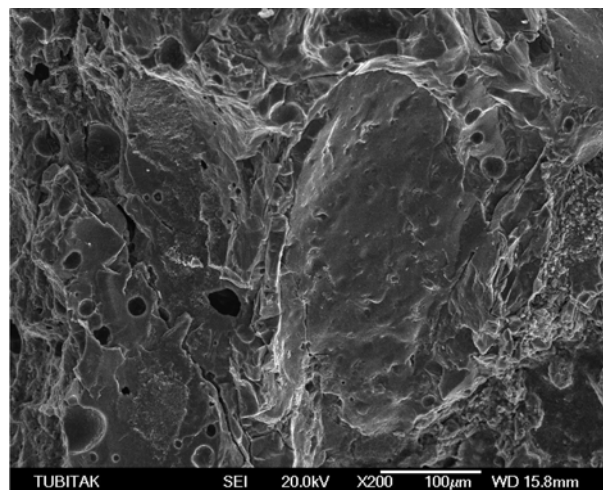


Fig. 13. Partial melting and large pores in MT-3 at 1200 °C for 3 hours.

but it is not easy to produce single phase cordierite ceramics with low thermal expansion coefficients. Due to multiple phases and especially, cristobalite the thermal expansion coefficient was higher but even in this form very useful cordierite-containing ceramics can be produced by using natural raw materials.

The addition of B_2O_3 to talc-based cordierite ceramics is very effective in reducing the cordierite formation temperatures and on the sintering behavior. This allows the production of ceramics with a high content of the cordierite phase at lower temperatures.

The addition of B_2O_3 to the talc-kaolin-alumina system for cordierite phase formation was found useful and reduced the cordierite formation by around 150 °C, from 1200 to 1050 °C with the addition of 3 wt% B_2O_3 .

On the other hand, the addition of B_2O_3 to the system at a higher content at higher temperatures ruined the Cordierite samples by causing partial melting and bloating.

All the results showed that, pure cordierite formation is not easy when impure raw materials were used and also the addition of B_2O_3 should be around 1 wt% for high temperature sintering and production of cordierite-containing ceramics.

Also, it was observed that, the sintering time was less effective in the sintering behavior of the system compared to the sintering temperature and B_2O_3 additions.

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