

Sintering behavior and properties of sepiolite-based cordierite compositions with added boron oxide

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Received: 09.08.2010

Abstract

This paper describes the sintering behavior and some properties of sepiolite-based cordierite ceramics with the addition of boron oxide at up to 3% wt. Sepiolite, kaolin, and alumina were used to prepare cordierite compositions in the cordierite phase area in a MgO-Al₂O₃-SiO₂ system with an excess amount of CaO and some Fe₂O₃ that basically came from sepiolite. Sintering of the dry-pressed samples was carried out at 850-1200 °C with a sintering time of 3 h. Sintered samples were characterized by XRD and SEM analysis, density, porosity, thermal expansion coefficient, shrinkage, and flexural strength measurements. The results showed that the addition of boron oxide reduced the cordierite formation temperature by about 100 °C and also reduced the sintering temperatures. The results also showed that the densification increased with increasing sintering temperatures up to 1100 °C, but above that temperature, partial melting began to occur in the samples, especially with larger additions of boron oxide.

Key Words: Sepiolite, sintering, cordierite, natural raw materials

1. Introduction

Sepiolite is a clay mineral that has a general formula of Si₁₂Mg₈O₃₀(OH)₄(H₂O)₄.8H₂O. It consists of fibrous talc-like layers stacked in long ribbons with microchannels and grooves parallel to the fiber axis. It was reported that in the structure of sepiolite, there are 3 groups of water molecules: zeolitic water, bound water, and hydroxyl water (Nagy and Bradley, 1955). Sepiolite is abundant in Turkey, and due to its chemical composition, it is a suitable raw material for production of cordierite-based ceramics with or without other raw materials. Günay (1999) carried out extensive work on Turkish sepiolites, especially their use in porous ceramic production.

There are a considerable number of studies on pure sepiolite minerals devoted to structural analysis, surface and adsorption characteristics, dehydration behavior, rheological and catalytic properties, and other physicochemical characteristics. The sintering behavior of sepiolite minerals was studied in detail by the present author (Gunay and Ozkan, 2001) to produce porous ceramic materials. Based on these experiences, the use of sepiolite in ceramic production, especially in cordierite ceramics, was considered. There have been some works on the use of natural raw materials in the production of some technical ceramics, and one of the most often considered materials is a cordierite composition in a MgO-Al₂O₃-SiO₂ system with some impurities.

The compound cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$) (2.2.5) was first reported by Rankin and Merwin (1918) in their classic work on the ternary system of $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$.

Cordierite powders can be prepared by the solid-state reaction of stoichiometric amounts of oxides of magnesium, aluminium, or silicon, or by glass recrystallization (Sumi et al., 1998). Extensive work has been carried out by many authors in the area of natural mineral resources on the raw materials for the preparation of cordierite. In industrial production of cordierite ceramics such as refractory applications, natural raw materials are often used. Some of the starting raw materials reported in the literature include a mixture of magnesium compounds and kaolinite (Kobayashi et al., 2000); alkaline-earth aluminosilicate glass, kaolin, alumina, and magnesite (Tulyaganov et al., 2002); talc, calcined alumina and fly-ash, kaolin, talc, silica, and alumina (Gonzales et al., 1999); talc, kaolinitic clay, and gibbsite (Tamborenea et al., 2003); talc, kaolin, and magnesium oxide (Yamuna et al., 2004); and talc, kaolin, sepiolite, and feldspar (Acimovic et al., 2003).

Cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$) is mainly used in glass-ceramic compositions utilized in multilayer electronic circuits, sound insulating boards, filters for separating solids from fluids, substrate material for catalytic converters, kiln furniture, and thermal insulation materials requiring controlled porosity (Tummala, 1985).

The aim of the present study was to use sepiolite with a high magnesium content in the production of cordierite ceramics, and also to add boron oxide to a mixture containing sepiolite, talc, and alumina to see its effect on the sintering behavior and properties of cordierite ceramics.

2. Experimental

Sepiolite (brown-colored sepiolite from the Eskişehir region of Turkey), kaolin (Kalemaden, Turkey), boric acid (Eti Maden, Turkey), and alumina (A16 SG, Alcoa, USA) powders were used as the raw materials to prepare batch compositions of cordierite ceramics with various amounts of B_2O_3 additions. Table 1 gives the chemical compositions of all of the starting raw materials. The chemical analysis of the raw materials was determined by XRF (X-ray fluorescence spectrometer, Philips PW 2404 WDXRF). The crystalline phases in sepiolite are sepiolite ($\text{Mg}_4\text{Si}_6\text{O}_{15}(\text{OH})_2 \cdot 6\text{H}_2\text{O}$) and dolomite ($\text{CaMg}(\text{CO})_3$), the crystalline phase in alumina is corundum ($\alpha\text{-Al}_2\text{O}_3$), and the crystalline phase in kaolin is kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$).

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

| | MgO | Al ₂ O ₃ | SiO ₂ | CaO | Fe ₂ O ₃ | TiO ₂ | Na ₂ O | K ₂ O | B ₂ O ₃ | LOI |
|------------|-------|--------------------------------|------------------|------|--------------------------------|------------------|-------------------|------------------|-------------------------------|-------|
| Sepiolite | 19.45 | 1.38 | 44.86 | 6.20 | 0.65 | 0.07 | 0.10 | 0.29 | - | 27 |
| 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 | - | - | - | - | - | - | - | - |

The composition of the cordierite ceramics in the present work was in the lower part of the cordierite area in the $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ system, as shown in Figure 1. Cordierite compositions were prepared by adding 0%, 0.5%, 1%, 2%, and 3% wt B_2O_3 to 100 g batches, and were coded as MS-0, MS-0.5, MS-1, MS-2, and MS-3, respectively.

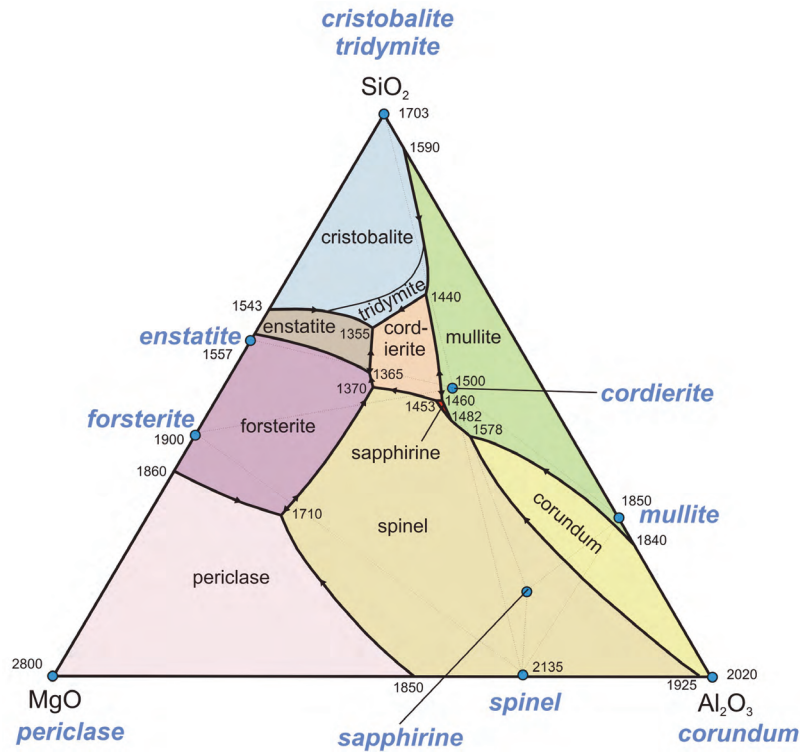


Figure 1. MgO-Al₂O₃-SiO₂ phase diagram.

Batch preparation was carried out by ball milling the dried raw materials for 3 h in porcelain jars with alumina balls. The phases in the dried batch were sepiolite, corundum, kaolinite, and dolomite, as expected.

Dry-pressing of all samples was carried out by using uniaxial pressing in steel dies with a pressure of 1 t/cm². Rectangular bars were pressed for the sintering studies.

Sintering experiments were carried out in static air for 3 h with a heating rate of 5 °C/min. Sintering temperatures were between 850 and 1200 °C.

The phase development of 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, employing a crosshead speed of 0.5 mm/min. 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 by applying the Archimedes principle in boiling water. Shrinkages in length and in thickness were measured from the dimensions.

Thermal expansion coefficients (TEC) of the sintered samples were measured by using a dilatometer (NETZSCH 402C/3/F) at up to 1000 °C in static air.

Microstructural characterizations of the samples were carried out with a scanning electron microscope (JEOL/SEM-6335F with INCA-EDS).

3. Results and discussions

Figures 2a and 2b show the shrinkage of the MS samples against sintering temperature with a sintering time of 3 h. It can be seen in the Figure that the shrinkage values in thickness were almost twice that of the shrinkage values in length of the bar shape samples. At 1100 °C, the shrinkage value in thickness was 18%, and that in length was 9%. The reason for this behavior is that, due to the sepiolite and kaolin, there was an alignment of the clay particles and sepiolitic fibers in dry-pressing, perpendicular to the pressing directions. Similar behaviors were also observed in sepiolite, by Gunay (1985) in spray-dried electrical porcelain granules and by Gunay and Ozkan (2001) in 2 different sepiolite minerals. The alignment of clay particles and sepiolitic fibers affected the shrinkage behavior and the amount of shrinkage.

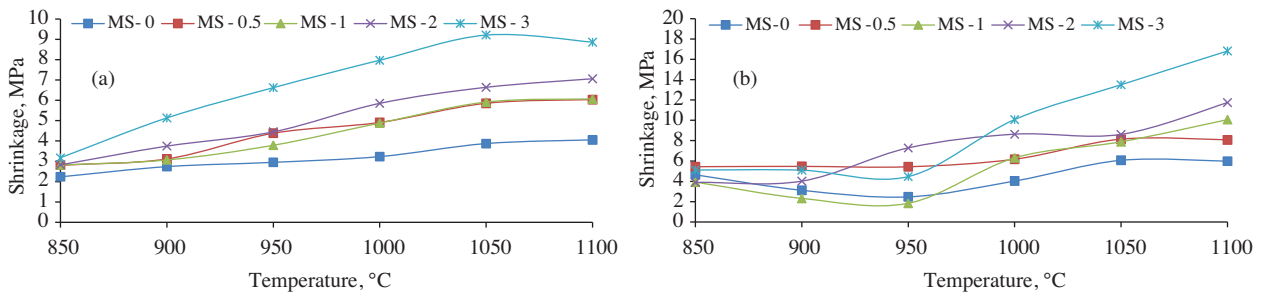


Figure 2. Linear shrinkages of cordierite ceramics a) in length and b) in thickness with increasing sintering temperatures.

It can be seen in the Figure that the amount of shrinkage increased with increasing sintering temperatures. It is also seen in the Figure that the amount of shrinkage increased with increasing B_2O_3 content, and, as expected, the highest shrinkage values were in ceramics with 3% wt B_2O_3 additions. After 1050 °C, it was observed that there was a decrease in the shrinkage value of MS-3; this behavior could be explained by the start of bloating in the MS-3 sample. This was also the result in sintered densities, which increased with sintering temperatures and B_2O_3 content, as shown in Figure 3. The fluctuations in the densities were probably due to the samples, because density measurements were carried out by using the samples after 3-point bending tests. Some cracks could have been in the samples and this could have affected the densities. Due to the partial melting in cordierite ceramics with 2% and 3% B_2O_3 content, the densities were not measured above 1100 °C. At higher sintering temperatures, the highest densities were obtained in samples with lower boron oxide content because of the partial melting and bloating in the samples, especially in those with higher boron oxide content. Photographs of these bloated and unbloated samples are shown in Figures 4a and 4b. In Figure 4a, bloating in MS-3 at 1200 °C can be seen clearly, but in the same sample, no bloating was observed at 1100 °C.

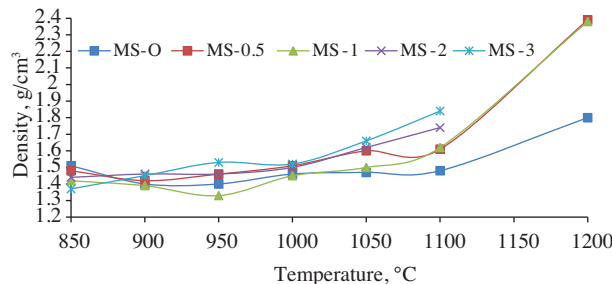


Figure 3. Densities in cordierite ceramics with increasing sintering temperatures.



Figure 4. a) Bloating in MS-3 at 1200 °C, b) no bloating in MS-3 at 1100 °C.

Figure 5 shows the effect of sintering temperature and boron oxide content on the porosities of sintered sepiolite-based cordierite ceramics. As expected after the density behavior, the values of porosities decreased with increasing temperatures and also with increasing boron oxide content. Again due to the partial melting and bloating at 1200 °C, porosities in MS-2 and MS-3 were particularly not measured properly. At 1200 °C, it could be seen that the values of porosity were around 38%, 13%, and 12% for MS-0, MS-0.5, and MS-1, respectively. At 1100 °C, all samples could be compared, as the shrinkage values were around 50% for MS-0, 45% for MS-0.5, 44% for MS-1, 42% for MS-2, and 33% for MS-3. These results also showed that the B_2O_3 addition was very effective on the sintering behaviors of sepiolite-based cordierite ceramics.

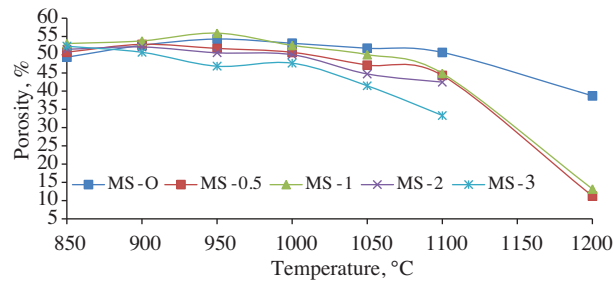


Figure 5. Porosities of cordierite samples with increasing sintering temperatures.

The flexural strength of MS cordierite ceramics also increased with increasing sintering temperatures and B_2O_3 content up to 1100 °C. It can be seen in Figure 6 that the flexural strength values increased gradually up to 1100 °C, and at this temperature, the lowest flexural strength was that of MS-0 and the highest value was that of MS-3, as expected after seeing the porosity and density values. B_2O_3 content was higher in MS-2 and MS-3, and partial melting and bloating at higher temperatures occurred in samples with higher B_2O_3 content. Samples with lower B_2O_3 content, such as MS-0, MS-0.5, and MS-1 showed increases in densities with increasing sintering temperatures; due to these higher densities, the flexural strength values increased with increasing sintering temperatures. Above 1100 °C, the flexural strength values of MS-2 and MS-3 could not be measured properly due to the partial melting and bloating. The flexural strength values of MS-0, MS-0.5, and MS-1 at 1200 °C were measured as approximately 23 MPa for MS-0, approximately 28 MPa for MS-0.5, and approximately 35 MPa for MS-1. Flexural strength values were high at lower sintering temperatures when the B_2O_3 content was high. At higher sintering temperatures, such as those above 1050 °C, the flexural strength values were high in samples with lower B_2O_3 content; the highest flexural strength value was obtained in MS-1 at 1200 °C, around 35 MPa.

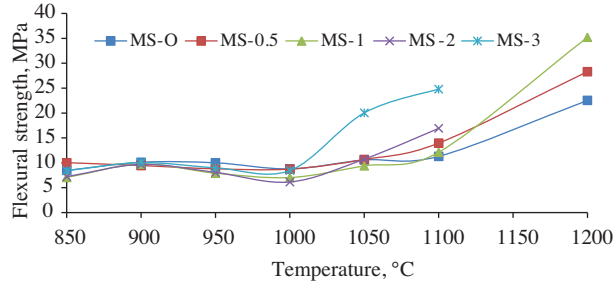


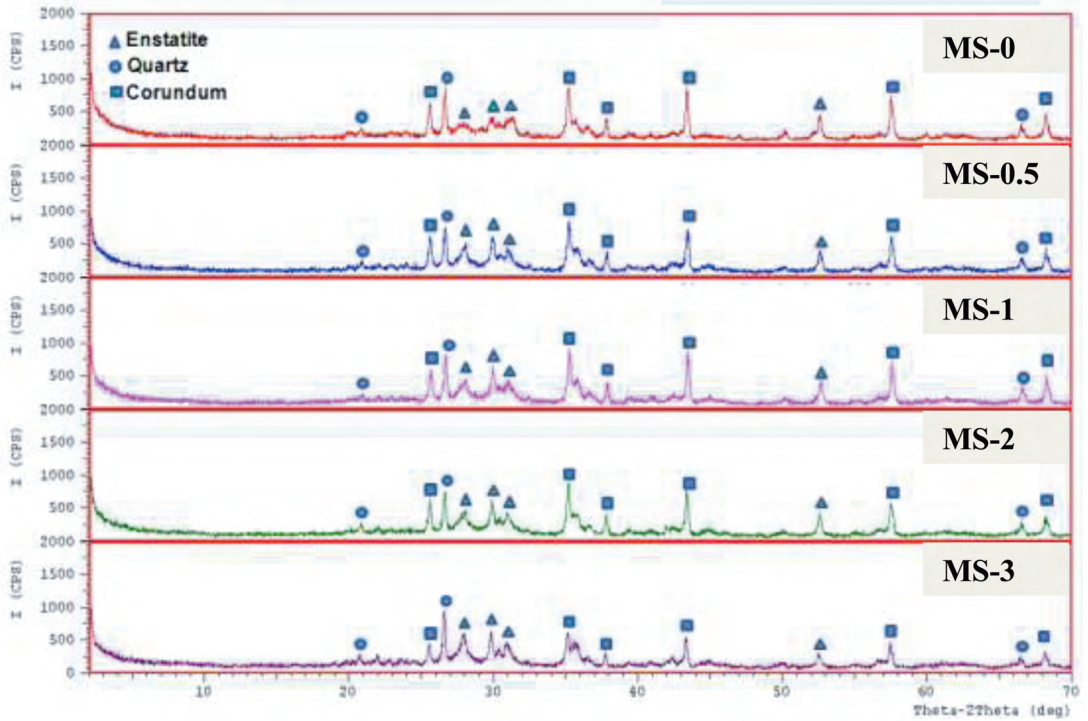
Figure 6. Flexural strength of cordierite ceramics with increasing sintering temperatures.

XRD analysis showed that MS cordierite ceramics contain corundum (Al_2O_3), enstatite ($\text{MgO} \cdot \text{SiO}_2$), cristobalite (SiO_2), cordierite ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$), and forsterite ($2\text{MgO} \cdot \text{SiO}_2$) as crystalline phases at the sintering temperatures of 900 and 1200 °C (Table 2 and Figure 7). In Table 2, the crystalline phases of MS ceramics at different temperatures for 3 h of sintering time are given. For a more detailed explanation, the same results are given as XRD patterns for the same sintering temperatures and time in Figures 7a (900 °C), 7b (1000 °C), 7c (1100 °C), and 7d (1200 °C). For correct comparisons of the XRD peaks, care was given to ensure that the counting and 2θ values were the same in all Figures. The important detail in the phase development was that the addition of B_2O_3 in cordierite ceramics influences the formation of the cordierite phase and reduces the cordierite formation temperature to 1100 °C, compared to 1200 °C in the sample without B_2O_3 content. The highest TEC value was in MS-3, $9.14 \times 10^{-6} / ^\circ\text{C}$, and the other samples with various B_2O_3 contents had similar TEC values, around $8.52 \times 10^{-6} / ^\circ\text{C}$. These TEC values were quite high for cordierite ceramics, but as shown in the XRD results, there are several phases in MS ceramics and cristobalite has an especially large effect on the TEC values in the system because of its high TEC value of around $10 \times 10^{-6} / ^\circ\text{C}$ (Kingery, 1960; Aumento, 1966). It is well known that cristobalite increases the TEC values of ceramic systems, and it was reported by Kobayashi et al. (2005) that cristobalite formation is very effective on the TEC values of $\alpha\text{-Al}_2\text{O}_3$ reinforced porcelain bodies. Around 30%-40% of quartz addition to the body resulted in TEC values of around $7.5 \times 10^{-6} / ^\circ\text{C}$. In the present study, the total amount of cristobalite and quartz phases (TEC approximately $14 \times 10^{-6} / ^\circ\text{C}$) was around 22% and the amount of corundum was around 38% after sintering at 1100 °C. The amounts of the phases were calculated by using the ratios of the maximum peak heights. The corundum ($\alpha\text{-Al}_2\text{O}_3$) phase had large TEC values ($8.8 \times 10^{-6} / ^\circ\text{C}$) in the system. The high TEC values in MS ceramics can be justified by considering the high amount of cristobalite and corundum phases present.

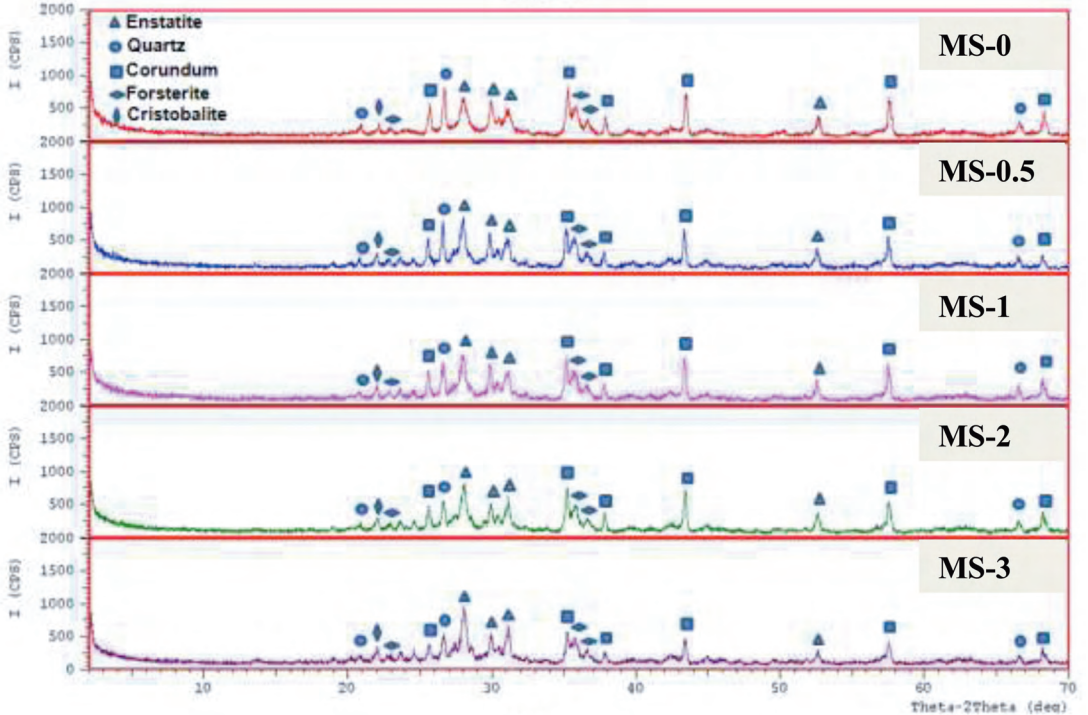
Table 2. Crystalline phases observed in sintered MS ceramics with various amounts of B_2O_3 content at various sintering temperatures.

| | 900 °C, 3 h | 1000 °C, 3 h | 1100 °C, 3 h | 1200 °C, 3 h |
|--------|-------------|--------------|----------------|------------------|
| MS-0 | C+Q+E | C+Q+E+F+Cr | C+E+Q+F+Cr | E+C+Cr+Cor+F |
| MS-0.5 | C+Q+E | C+Q+E+F+Cr | C+E+Q+F+Cr+Cor | E+C+Cr+Cor+F |
| MS-1 | C+Q+E | C+Q+E+F+Cr | C+E+Q+F+Cr+Cor | E+C+Cr+Cor+F |
| MS-2 | C+Q+E | C+Q+E+F+Cr | C+E+Q+F+Cr+Cor | Partially melted |
| MS-3 | C+Q+E | E+C+Q+F+Cr | C+E+Q+F+Cr+Cor | Partially melted |

C: corundum, E: enstatite, Q: quartz, Cr: cristobalite, F: forsterite, Cor: cordierite



(a)



(b)

Figure 7. Crystalline phases observed in sintered MS ceramics with various amounts of B₂O₃ contents at a) 900 °C, b) 1000 °C, c) 1100 °C, and d) 1200 °C sintering temperatures for 3 h.

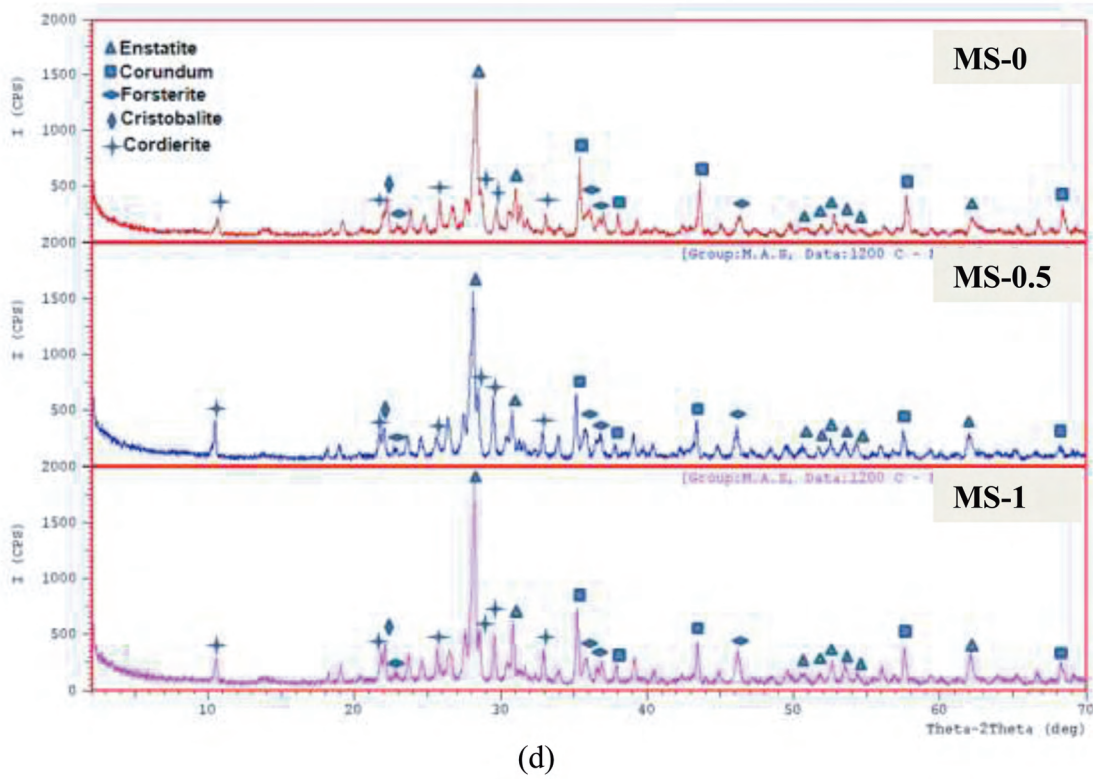
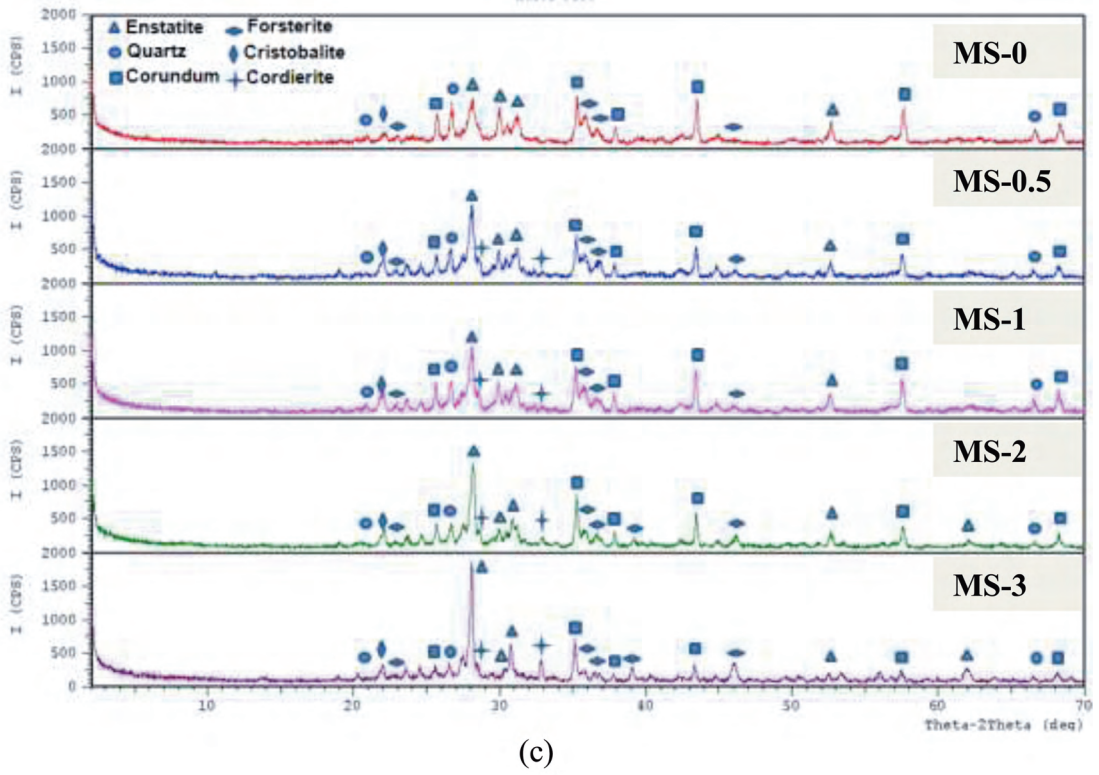


Figure 7. Continued.

Microstructural investigations by SEM also revealed that there are multiple phases in MS cordierite ceramics. The cordierite regions are the most reacted regions, and sepiolite reacts with kaolin and alumina to form cordierite. Sepiolite is also the source of enstatite phases. 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 as XRD results revealed, there are cristobalite phases in MS 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. This behavior and the detailed phase development in this system will be the subjects of another publication.

In Figure 8, the beginning of partial melting is shown in MS-3 at 1100 °C for 3 h. It can be seen that the bloating had just begun, and some large pores are visible in the microstructure. In the MS-3 system (with 3% wt B_2O_3 addition), partial melting and bloating was extended and the samples were bloated above the sintering temperatures of 1100 °C. Due to this, no measurements were carried out.

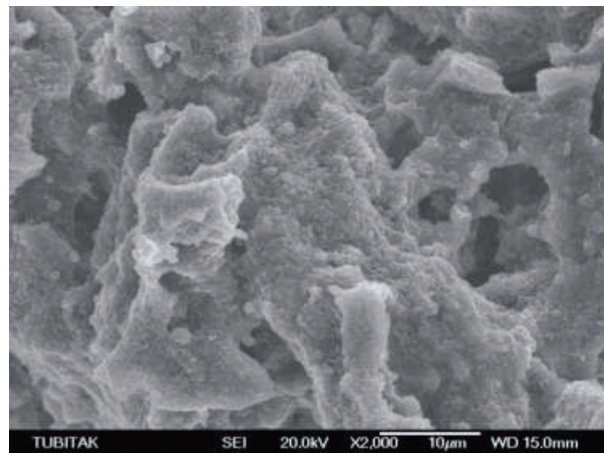


Figure 8. SEM micrograph of the partial melting in MS-3 at 1100 °C for 3 h.

4. Conclusions

The use of natural raw materials in the preparation of cordierite ceramics is very important in an economic sense, 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. In the case of sepiolite, it is very convenient to produce cordierite-based ceramics low in density and high in porosity for absorption and heat-insulating properties. This study is especially important for Turkey because there are abundant sepiolite sources with various properties there.

The addition of B_2O_3 to sepiolite-based cordierite ceramics is very effective in reducing the cordierite formation temperatures and on the sintering behavior. This allows for the production of ceramics with high contents of cordierite phases at lower temperatures.

Acknowledgements

The author wishes to thank Yusuf Öztürk, Hidayet Bodur, Emre Karabeyoğlu, and Bayise Vatanserver for their help during the course of this research.

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