Original article

Synthesis, characterisation and sintering behaviour influencing the mechanical, thermal and physical properties of cordierite-doped TiO$_2$

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A R T I C L E   I N F O

A B S T R A C T

Cordierite–TiO$_2$ composite (5–20 wt.%) ceramics for various stoichiometric compositions were synthesised using conventional techniques with standard raw materials. The green composite ceramic samples obtained were dried at 100 °C for 12 h, followed by pre-sintering at 800 °C for 3 h. The powders were dry milled for 2 h and then compacted at 240 MPa to form pellets. The sample pellets were sintered at temperatures in the range of 600–1300 °C for 3 h. The study of the different phases of the samples was performed using X-ray diffraction. The poor mechanical properties of cordierite have attracted the use of TiO$_2$ as a dopant. A study on the influence of TiO$_2$ addition to flexural strength, fracture toughness, hardness, bulk density and thermal expansion was performed. Vickers hardness value of the cordierite–TiO$_2$ composites of 6.46 GPa is higher than other compositions of cordierite. The cordierite–TiO$_2$ exhibited a fracture toughness of 3.28 MPa m$^{1/2}$. The flexural strength of the cordierite–TiO$_2$ was 158.47 MPa. The effect of thermal expansion was very low in the cordierite–TiO$_2$. Studies using X-ray diffraction and scanning electron microscope imaging on samples sintered at 1300 °C confirmed the presence of cordierite, along with small amounts of rutile and cristobalite.

1. Introduction

Cordierite (2MgO–2Al$_2$O$_3$–5SiO$_2$) ceramics possess unique properties, such as a low dielectric constant and thermal expansion and a high refractoriness, which make the material a potential candidate for industrial applications [1–5].

Numerous techniques have been used for the synthesis of cordierite, such as conventional and sol–gel techniques by mixing powders and using solutions. Another technique for the preparation of cordierite is from the field of glass ceramics, in which powders are heated above their melting points.

In engineering applications, the mechanical properties of materials play a major role in determining their suitability for

specific applications. These mechanical properties are related to the crystalline phase and microstructures of the materials. Desirable properties of ceramic systems can be obtained by the proper selection of the stoichiometric composition required for the formation of the crystalline phases. Development of fine-grained microstructures in ceramics improves the thermo-mechanical properties [6]. The formation of ceramics is influenced by the composition, the choice of nucleating agents, and the heat treatment processes used [7].

The present study on cordierite focussed on the fabrication of ceramic matrix composites for high temperature applications. Recent attention has been given to the addition of suitable dopants, such as zirconia, ceria, titania, yttria, and silicon carbide for improvements in the mechanical properties of ceramics. Many researchers have reported increased the hardness and improved the properties of ceramic materials, such as in the achievement of a high-Young modulus and a very low coefficient of thermal expansion [8–10]. One such improved ceramic, cordierite, is considered as an alternate for conventional reinforcing glass fibres in high-temperature advanced composite applications.

The addition of TiO_2 to glass [6,10] followed by a heat treatment at 1100 °C for 2 h produced very good mechanical properties and yielded a maximum value for the elastic modulus and the hardness. The TiO_2 dopant added to the cordierite enhanced the mechanical and thermal properties and the crystalline phase formation. TiO_2 is soluble in the molten glass and readily precipitates during heating and cooling. The nucleating agents used for cordierite ceramics are TiO_2 combined with zirconia [10]. TiO_2 is further responsible for glass separation, which leads to crystallisation.

A report on a novel mixed-oxide of strontium/calcium-feldspar ([Sr/Ca]O·Al$_2$O$_3$·2SiO$_2$)–aluminium-titanate (Al$_2$O$_3$·TiO$_2$) describes a system developed for diesel particulate filters. The highly developed micro cracked structure and lower thermal expansion of the ceramic were stated as the reason for the high thermal shock resistance of the mixed-oxide material. The addition of TiO_2 produced an increase in fracture toughness and hardness of the material. Reports in the literature can be found that describe the crystallisation process of cordierite using TiO_2 as a nucleating agent. Reports have also examined the relationship between the nucleation and the crystallisation of cordierite [11]. In the TiO_2–zirconia–mullite composite, ceramics have been fabricated by in situ controlled crystallisation of Si–Al–Zr–O amorphous bulk [12].

Our literature review found only a few papers dealing with the study of the mechanical properties of cordierite–TiO_2 ceramics [10,12]. This study describes the simple approach for the fabrication of cordierite doped with TiO_2 (5–20 wt.%) through the use of a conventional technique of heat treatments at various sintering temperatures. Characterisation of the mechanical and thermal properties of the cordierite–TiO_2 dopant is reported in this paper.

2.   Experimental work

Cordierite–TiO_2 (5–20 wt.%) composites were prepared using conventional techniques. The cordierite powders of stoichiometric composition (MgO 13.8; Al$_2$O$_3$ 34.8; and SiO$_2$ 51.4) were
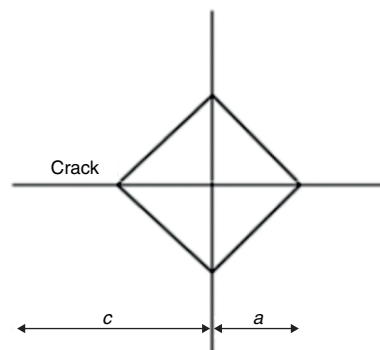

Fig. 1 – Representation of the fracture toughness measurement procedure.

mixed thoroughly with TiO_2 powder with varying compositions (5 wt.%, 10 wt.%, 15 wt.% and 20 wt.%, which are referred to as CTi05, CTi10, CTi15 and CTi20 for the noted dopant additions, respectively). Mixed raw powders were milled for 2 h to obtain better homogeneity. The ceramic powders were mixed with a polyvinyl alcohol binder and compacted at 240 MPa to form 10-mm diameter pellets. The precursors were sintered at various temperatures ranging from 600 to 1350 °C for 3 h. The sintered samples were then polished with different grades of polishing papers. Characterisation of the samples using X-ray powder diffraction analysis (SEIFURT) was performed using graphite monochromatic Cu Kα radiation from an X-ray tube operating at 30 kV and 40 mA. The XRD patterns were acquired in the 2θ range of 5–70° to determine the evolution of phases at different sintering temperatures. Indentation hardness testing was performed for different loads using a Vickers hardness tester. Accurate measurement of the hardness requires a well-defined indentation, for which the specimen needs the surface to be prepared by grinding and polishing. The Vickers hardness, HV, is found using the formula

$$HV = 1.854 \frac{P}{d^2}$$

where P is the indentation load (N) and d is the mean diagonal (m).

Fracture toughness (KIC) was evaluated using the indentation fracture method. KIC of the ceramics was estimated for a load (98 N), assuming 15 s as the holding time, using the following formula with a Vickers indenter.

$$KIC = 0.0319 \frac{P}{al^{1/2}}$$

where P is the indentation force (N), c is the crack length (m), and a is the half length of the diagonal (m), $l = c - a$, as described in Fig. 1.

The span length of a 25-mm long sample was prepared to measure the flexural strength. The measurements were performed using the three-point bending technique performed using a universal testing machine. The cross speed in loading was 0.5 mm/min. Thermo-mechanical analysis was conducted to measure the coefficient of thermal expansion in a dilatometer (VB model: from 70 to 800 °C at a heating rate of 10 °C/min). The micro-structural features of the samples were observed using scanning electron microscopy. Thermal
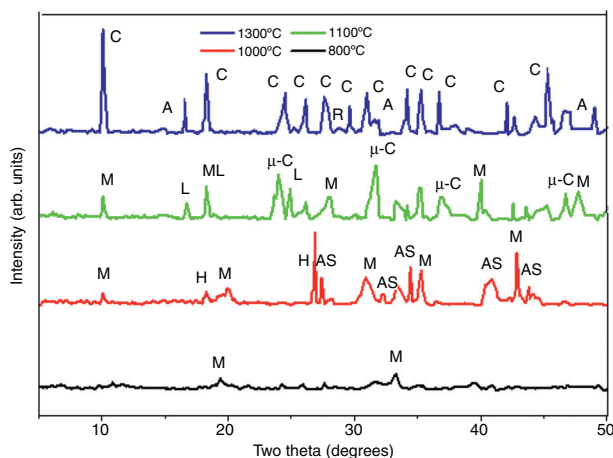
Fig. 2 – XRD patterns of cordierite–TiO$_2$ (CTi10) powder samples sintered at different temperatures.

etching was performed for the samples at 1100 °C and covered with gold coated by an ion sputtered method. The density was measured using Archimedes' principle.

3.   Results and discussion

The different cordierite–TiO$_2$ (CTi05, CTi10, CTi15 and CTi20) ceramic composites were characterised for their mechanical properties and thermal properties after processing under heat treatments at different sintering temperatures in the range of 800–1300 °C for 3 h. The consolidated results of XRD for different sintering temperatures are listed in Table 1.

3.1.   Microstructure of cordierite–TiO$_2$

The XRD patterns recorded for the heated treated samples at various sintering temperatures (800, 1000, 1200 and 1300 °C) are shown in Figs. 2 and 3. The XRD peak locations were verified with the standard ICDD (International Centre for Diffraction Data) data using JCPDS (Joint Committee on Power Diffraction Data) software. The XRD patterns of
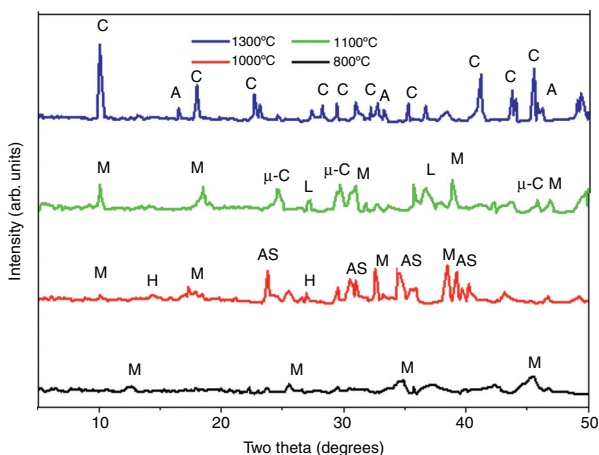

Fig. 3 – XRD patterns of cordierite–TiO$_2$ (CTi20) powder samples sintered at different temperatures.

sintered samples CTi10 and CTi20 confirms the start of a solid state reaction and its phase changes under the various sintering temperatures. The XRD pattern at 800 °C exhibits the weak diffraction patterns representing a small amount of crystalline phase at 19 and 32 (2θ) that were identified using JCPDS card 5-450 for magnesium aluminium titanate (M). This result confirms the work of Shamsudin et al. [6], who reported the formation of magnesium aluminium titanate at 850 °C, and the work of Quyang et al., who reported this formation in the temperature range 850–900 °C. The heat treatment at 1000 °C revealed the formation of new compounds 19–769 for a high quartz solid solution (H) represented at 27, magnesium aluminium silicate (AS) along with magnesium aluminium titanate during the initial stages of crystallisation [11]. However, the sintering process is not complete until the formation of stable cordierite phases that occur due to the reaction between the amorphous silica and high quartz solid solution and the magnesium aluminium silicate that causes the density to increase with increasing sintering temperatures. The diffractogram at 1100 °C revealed metastable and stable phase cordierite along with magnesium aluminium titanate, cristobalite and rutile, with sharp peaks and high intensities. At the final sintering temperature of 1300 °C, stable cordierite became the main crystalline phase, as indicated by the sharp peaks and high intensities compared with the samples at the sintering temperature of 1100 °C. The presence of stable-phase cordierite, along with aluminium titanate, was observed. These reported results were consistent with the work of Wange et al. [9], who reported the formation of stable-phase cordierite along with aluminium titanate at 1200 °C.

To conclude, the advantages of milling and higher soaking time have been demonstrated by the obtained results. The powders during synthesis at 800 °C exhibited amorphisation relative to the results of the XRD and DTA studies. However, the cordierite synthesis effectiveness was confirmed with the addition of TiO$_2$. The investigation of the synthesis of cordierite by experimental methodology demonstrated a clear conclusion from the data. The present experimental investigation found that cordierite is synthesised at 1300 °C. Note that the difference between sintering time and synthesis temperature found and recorded by Pinera et al. is substantial [12]. It is hoped that this reduced synthesis temperature of cordierite from 1420 °C was due to the presence of TiO$_2$ as a dopant. This reduced synthesis temperature demonstrated that the TiO$_2$ presence accelerated the phase transformation kinetics. Hence, the combined effect of milling and dopant addition has led to the decrease in the cordierite synthesis temperature. The compounds of TiO$_2$ and SiO$_2$ do not form reaction products; instead, they form a high viscosity liquid separately. Hence, this has been a strong contender for the cordierite formation and confirms that the TiO$_2$ does not affect the cordierite formation. This transformation clearly shows the disappearance of spinel is associated with the reaction of amorphous silica to α-cordierite.

The addition of TiO$_2$ in the cordierite synthesis demonstrated the effect of the sintering mechanism and its impact on the cordierite crystallisation. TiO$_2$ doping is very effective in reducing the cordierite formation temperatures and the sintering behaviour. In addition, the introduction of TiO$_2$ resulted

Table 1 – Phase evolution of samples sintered at various temperatures.

Samples	Phase composition			
	800 °C	1000 °C	1100 °C	1300 °C
Cordierite–TiO$_2$ (CTi05)	A	H M A S	α-Cμ-CLATCR	α-CATCR
Cordierite–TiO$_2$ (CTi10)	A	H M A S	α-Cμ-CLATCR	α-CATCR
Cordierite–TiO$_2$ (CTi15)	A	H M A S	α-Cμ-CLATCR	α-CATCR
Cordierite–TiO$_2$ (CTi20)	A	H M A S	α-Cμ-CLATCR	α-CATCR

A, amorphous; H, high quartz solid solution; M, magnesium aluminium titanate; AS, magnesium aluminium silicate; L, low quartz solid solution; α-C, cordierite (stable); AT, aluminium titanate; C, cristobalite; R, rutile.

in the excessive formation of aluminium titanate, a formation of secondary phases considered to be a means of enhancement of the mechanical properties. This work confirms the production of ceramics with high contents of cordierite phases at lower temperatures.

DTA analysis for the pre-heat treated samples of cordierite–TiO$_2$ (CTi10) shown in Fig. 4 exhibited the following results. The endothermic peak was observed in two regions in both the samples. The first exothermic peak, at a temperature of approximately 884 °C, describes the initiation of the solid state reaction that leads to the phase transformation. The second exothermic peak at 1134 °C confirms the crystallisation of μ-cordierite. The analysis concludes with the supporting results of the XRD patterns [11]. The results of DTA analysis by Shamsudin et al. [6] reported the same effect on the sintering behaviour as this investigation suggests, for instance, milling accelerates the reaction of formation of cordierite at lower sintering temperatures.

3.2. Properties of cordierite–TiO$_2$

The Vickers hardness of the cordierite–TiO$_2$ (CTi05-20) samples increases with an increase in the sintering temperature, as shown in Fig. 5. The hardness value of the samples sintered at 1100 °C exhibited an increase in hardness and was found to be decreasing with a further increase in the sintering temperatures. The reason for the increased hardness value at 1100 °C was due to the presence of the magnesium aluminium titanate phase
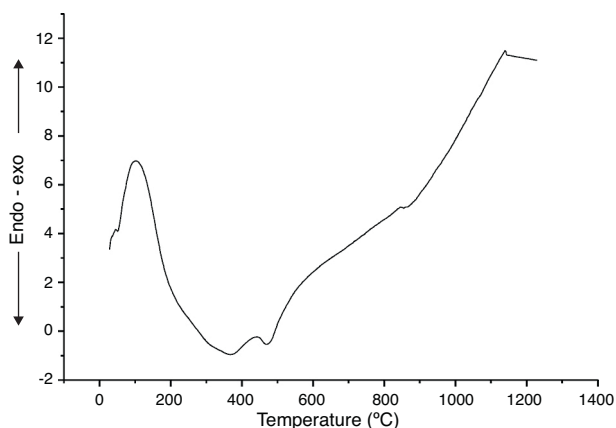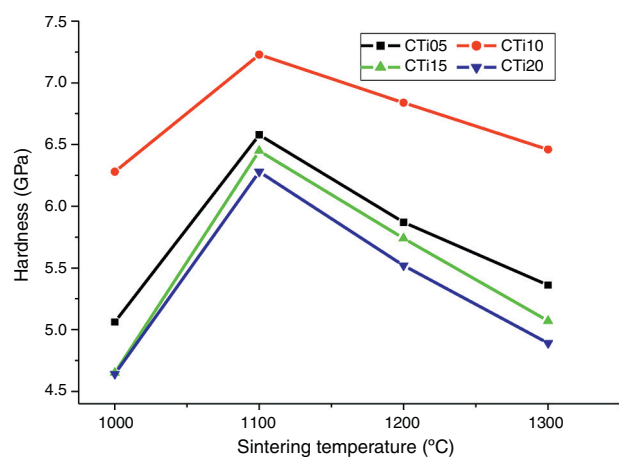

Fig. 5 – Vicker's hardness of cordierite–TiO$_2$ (CTi05-20) at different sintering temperatures.

in the samples. Further increase in the sintering temperatures resulted in a decreased hardness value. Moreover, the sample CTi10 exhibited a better hardness value of 6.46 GPa [12]. The samples CTi05 and CTi10 dissolved the TiO$_2$ dissolved in alumino-silicate, which reduced the formation temperature and enhanced the formation of the cordierite phase. The TiO$_2$ presence as a nucleating agent increased the size of the grains and further completes the grains with small amounts of cristobalite and rutile. With an increasing content of TiO$_2$ in cordierite (CTi10 and CTi20), the excess phase TiO$_2$ forms a different phase rutile along with cordierite phase. The presence of the secondary phases of rutile and aluminium titanate decreased the hardness value of cordierite–TiO$_2$ for different wt.% at higher sintering temperatures. Another reason that has been cited for the decreased hardness is due to the decrease in the cristobalite phase. The Vickers hardness value for the sample CTi10 at 1300 °C was found to be the highest (6.46 GPa) among all the other samples, as well as with pure cordierite.

Fig. 6 shows the optical image of a crack length observed at 98 N load, which developed due to indentations to estimate the fracture toughness. The fracture toughness plot for different temperatures of cordierite–TiO$_2$ (CTi10 and CT20) is shown in Fig. 7. The fracture toughness value at 1100 °C exhibited higher values due to the presence of a low quartz solid solution (L). Note that the coefficient of thermal expansion is higher compared to all the other phases. At this temperature, the
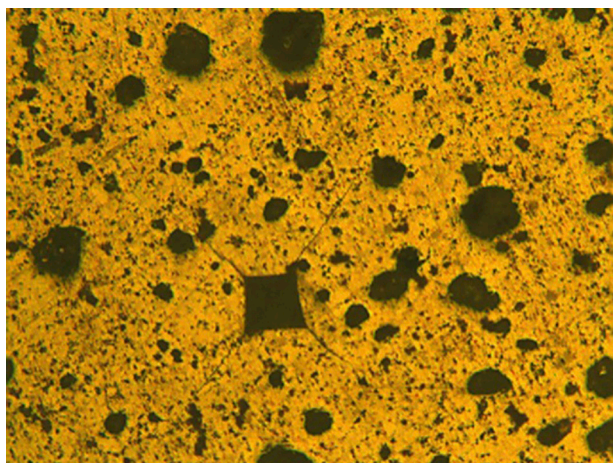

Fig. 4 – DTA curve for a cordierite–TiO$_2$ (CTi10) sample dried at 100 °C.

Fig. 6 – Optical micrographs of the typical identifying marks on a cordierite–TiO$_2$ (CTi20) sample sintered at 1300 °C.

Fig. 8 – Flexural strength of cordierite–TiO$_2$ (CTi10 and CTi20) sintered at different temperatures.

transformation of quartz phase cause high stresses to develop upon cooling. The stresses developed deflect the cracks, thus leading to increased fracture toughness. Above this temperature, the cordierite–TiO$_2$ (CTi05-20) samples exhibited a low fracture toughness value. The reason for the low toughness is the presence of TiO$_2$ as a nucleating agent, beginning with the precipitating and generation of a stress concentration in the matrix. The fracture toughness value for cordierite–TiO$_2$ (CTi10) of 3.28 MPa m$^{1/2}$ was higher than the CTi20 value of 2.81 MPa m$^{1/2}$, which exhibited a better result compared with the results obtained by Wange et al. [9] Cordierite–TiO$_2$ (Cti15 and CTi20) fracture toughness values were found to be lower than CTi10 and were due to the generation of a high stress concentration in the matrix, which was responsible for the acceleration of crack growth. The fracture toughness value of CTi10 exhibited a remarkably higher value compared to other compositions because the TiO$_2$ dissolved in the alumina silicate. This dissolving is responsible for reducing the transformation temperature of cordierite. Hence, the results indicate that the optimum cordierite–TiO$_2$ (CTi10) enhances the mechanical properties making it a suitable alternate
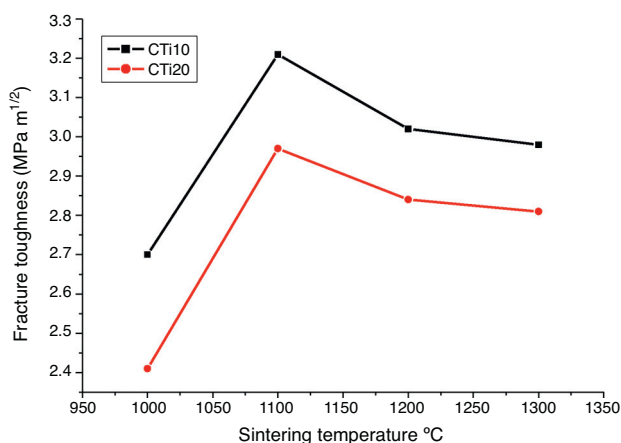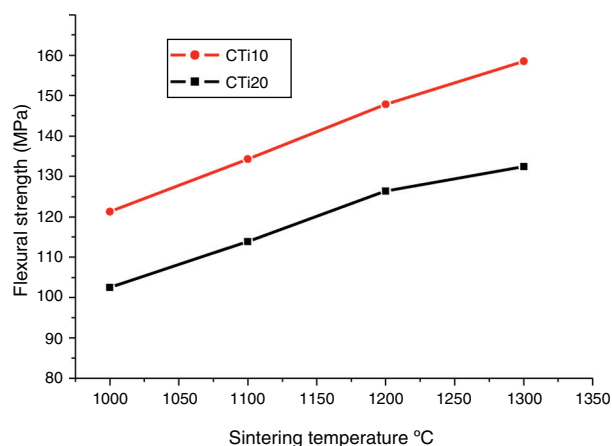
material for cordierite in high temperature applications. The studies involved the characterisation of the strength and the micro-structural features recorded for the various sintering temperatures. Our investigation demonstrated that pore size and its distribution plays a major role in the propagation of either macroscopic or microscopic cracks or processing defects, which affects the fracture toughness. Indeed, fracture toughness of cordierite–TiO$_2$ (3.28 MPa m$^{1/2}$) is much higher than that of dense cordierite bodies (2.878 MPa m$^{1/2}$) [8].

The flexural strength was determined for cordierite–TiO$_2$ (CTi10 and CTi20) composites that were heat treated at various sintering temperatures. The Cordierite–TiO$_2$ (CTi10) flexural strength was found to increase with increasing sintering temperature, due to the formation of α-cordierite at these temperatures. During the transformation process between low-quartz solid solution and α-cordierite, the thermal mismatch causes micro-cracks to be formed during the process of sintering. The flexural strength values obtained demonstrates the remarkable influence on the presence of these micro-cracks. However, the flexural strength values are influenced by the formation of cordierite. The TiO$_2$ addition into the cordierite enhanced the flexural strength and resulted in even higher results than those of Pinero et al. [13]. The cordierite–TiO$_2$ (CTi10) sample value of 158.47 MPa was found to be higher than that of CTi20, as shown in Fig. 8.

Fig. 9 displays the SEM images of the cordierite–TiO$_2$ (CTi20) sample sintered at 1300 °C. The increase in the sintering temperatures exerted a remarkable influence on the microstructure and morphology of the samples. The sintering process leads to the nucleation of crystals, thereby confirming two phases in the system in the form of spherical/droplet and glassy phases. The images indicate the TiO$_2$ appears in the form of irregular blocks. A decrease in pore volume with an increase in the sintering temperature is clearly evident from the sample with good densification. Heat treatment of the samples plays an important role on the characteristics of the microstructure and morphology of the cordierite ceramics.

The bulk densities as a function of the sintering temperature for the various heat-treated samples are shown in Fig. 10. The bulk density reached a maximum value at 1100 °C and
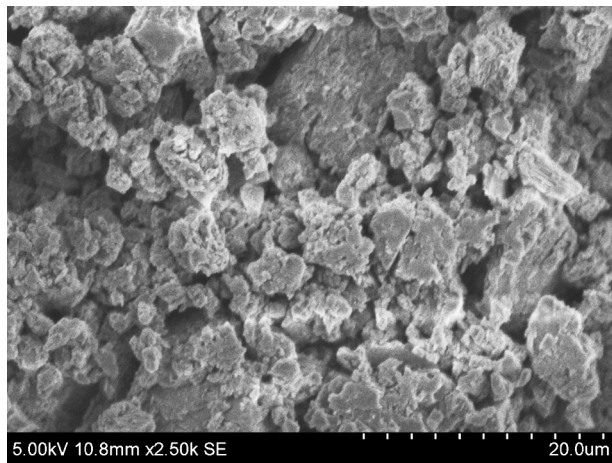

Fig. 7 – Fracture toughness of cordierite TiO$_2$ (CTi10 and CTi20) sintered at different temperatures.

Fig. 9 – SEM image of a cordierite–TiO$_2$ (CTi20) specimen sintered at 1350 °C for 3 h.

was found to decrease with an increase in the sintering temperature [6]. This behaviour was due to the transformation of α-quartz with more siliceous, indicating the contraction in volume. The further increase in sintering temperature causes the disappearance of prominent cordierite phases with the quartz phase. This disappearance causes a volume expansion, thereby causing the density to decrease. The excessive TiO$_2$ introduction produced an increase in density of the sample and the improved bonding performances of the sample. In this investigation, the phase development was observed in the precursor mixes at sintering temperatures well below that required for full cordierite formation at 1400–1440 °C [1,2]. In this paper, the sintering temperature was raised to 1300 °C, which significantly enhanced the formation of cordierite, until the densification process was completed. This sintering temperature is the temperature that is quite frequently reported in literature [6,8,9,13] on the formation of cordierite during heat treatment of powder precursors with the addition of a dopant.

The thermal expansion coefficient (TEC) for cordierite–TiO$_2$ (CTi10 and CTi20) composites heat treated at 1300 °C was performed using a dilatometer in the temperature range between 60 and 800 °C. It is well known that cristobalite increases the
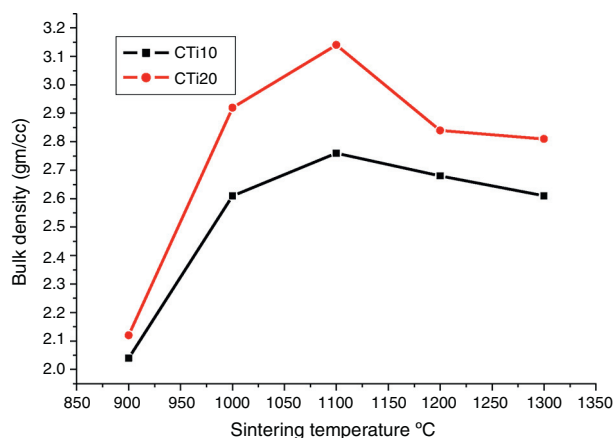

Fig. 10 – Bulk density of cordierite–TiO$_2$ (CTi10 and CTi20) samples sintered at different sintering temperatures.

TEC values of ceramic systems, as reported by Wange et al. [9]. The value of TEC at 477 °C was 14×10^{-6} and that at 537 °C was 7×10^{-6}, due to the presence of α-quartz and β-quartz. The values of TEC were higher during the transformation and confirm all the intermediate phases possess higher values of TEC. The cordierite, as a single phase with low thermal expansion, is not easy to synthesise; hence, the ability to use a dopant for synthesis was pursued in the present research. The growth with dopants caused the occurrence of multiple phases. The presence of these multiple phases, especially aluminium titanate, in cristobalite resulted in thermal expansion coefficient values that are slightly higher compared to pure cordierite (2×10^{-6}/°C). The thermal expansion coefficient for CTi10 and CTi20 are 3.61×10^{-6} and 5.09×10^{-6}/°C [13], respectively, at 800 °C, which indicates that α-cordierite is the major phase. However, this result was possible only due to the presence of cordierite as a major phase.

4. Conclusion

The study of cordierite synthesis with titanium dioxide was found to be rare; hence, with significant interest, this study focused on the synthesis of cordierite doped with titanium dioxide and the properties of the resulting ceramic material. The characterisation results of the mechanical properties and thermal properties for the samples CTi05, CTi10, CTi15 and CTi20 are as follows:

- The addition of TiO$_2$ in the cordierite formation was evident at the lowest sintering temperature used to form crystalline α-cordierite (1300 °C).
- The hardness value of the cordierite–TiO$_2$ (CTi10) exhibited a higher value than undoped cordierite.
- The fracture toughness value of cordierite–TiO$_2$ (CTi10) was high compared to the other samples studied.
- The flexural strength of cordierite–TiO$_2$ (CTi10) exhibited a value of 158.47 MPa; this is higher than cordierite–TiO$_2$ (CTi20).
- The composites exhibited a very low thermal expansion coefficient of 3.61×10^{-6}/°C.
- The cordierite–TiO$_2$ (10 wt.%) exhibited improved mechanical properties; these improved properties degraded with higher weight percentage addition of TiO$_2$.

The addition of titanium dioxide aided the sintering of the cordierite ceramics. The mechanical properties of the cordierite–TiO$_2$ samples resulted in a remarkable influence of TiO$_2$ as a dopant on the crystallisation process of cordierite. SEM analysis demonstrated the significant variation in morphology of the crystalline phases with the changes in the heat treatment temperatures.

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