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## **EFFECT OF HIGH TEMPERATURE TREATMENT ON THE PROPERTIES OF CORDIERITE- ZIRCONIA NANOCOMPOSITES**

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### **ABSTRACT**

Pure cordierite and cordierite - ZrO<sub>2</sub> composites containing 10, 20 and 30 wt% Y<sub>2</sub>O<sub>3</sub> stabilized ZrO<sub>2</sub> have been prepared by dispersing ZrO<sub>2</sub> powder in cordierite sol. The evolution of crystalline phases and the microstructure have been studied using X-ray diffraction and scanning electron microscopy. It was found that increasing both ZrO<sub>2</sub> content and firing temperature enhanced the bodies' density. Mullite net and rods crystallize in the composite matrix when it heat treated at 1450°C. The beneficial effects of mullite and ZrO<sub>2</sub> on the bending strength of the fabricated composites have been described.

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## INTRODUCTION

Cordierite ( $2 \text{ MgO} - 2\text{Al}_2\text{O}_3 - 5\text{SiO}_2$ ) is a very important compound with low thermal expansion coefficient, low dielectric constant and good chemical stability. It was first reported by Rankin and Merwin<sup>(1)</sup> in their classical work on the ternary system  $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ . In nature it occurs in thermally metamorphosed argillaceous rocks<sup>(2)</sup>. It can be prepared by sol-gel synthesis, liquid phase sintering, glass-ceramic route and solid state reaction<sup>(3-7)</sup>. Despite numerous advantages of cordierite, its narrow range of sintering temperature<sup>(8)</sup> and moderate mechanical properties are among the main drawbacks for its application as a thermal barrier material. According to Sano<sup>(9)</sup>, the addition of zircon in the magnesium aluminosilicate (MAS) system is an efficient way to widen the range of sintering temperature. Das Gupta et al<sup>(10)</sup> examined the effect of commercial  $\text{ZrO}_2$  both in unstabilized (m- $\text{ZrO}_2$ ) and 3Y-PSZ (mainly t, some m) form, on the thermal and mechanical properties of cordierite ceramics. They showed that the addition of  $\text{ZrO}_2$  improves the mechanical properties of cordierite ceramics with a simultaneous increase in dilation behavior, the extent of which is dependent on the crystalline form of  $\text{ZrO}_2$ .

Although dispersion of  $\text{ZrO}_2$  phase to another matrix has been used to improve mechanical properties, however, there was no significant improvement of mechanical properties and effect of sinterability until the dispersed amount of  $\text{ZrO}_2$  was more than 6 vol. %<sup>(11-15)</sup>. Sun et al<sup>(16)</sup>, and Hirano & Inada<sup>(17)</sup> toughened cordierite by dispersing 5 to 25 wt % and 15 to 35 wt%  $\text{ZrO}_2$  into cordierite matrix respectively. They concluded that the thermal expansion coefficient increases gradually with increasing  $\text{ZrO}_2$  content. The fracture strength, the toughness and the thermal shock resistance were increased also, with  $\text{ZrO}_2$  content. They attributed the toughening improvement to the transformation toughening. It is accepted that transformation toughening usually involves stress-induced martensitic transformation of  $\text{ZrO}_2$  particles from tetragonal (t-  $\text{ZrO}_2$ ) to monoclinic (m-  $\text{ZrO}_2$ ) symmetry in the stress field of a propagation crack; which in turn enhanced both fracture strength and fracture toughness<sup>(18)</sup>. Oliveira and Fernandes<sup>(18)</sup> stated that the addition of  $\text{ZrO}_2$  induced the formation of  $\text{ZrSiO}_4$  thus affecting densification, which resulted in substantial improvement in strength. They claimed that fracture toughness was affected by milling time. It increases with milling time, as a result of a better distribution of the  $\text{ZrO}_2$  particles and particle size reduction. On the other hand, Hirvonen et al<sup>(19)</sup> proved that the density of nanocomposite of zirconia and cordierite decreases with the rise of the sintering temperature of the green compacts with the equal amount of cordierite and that the all volume of cordierite (silica) reacted with  $\text{ZrO}_2$  during fabrication of pressureless sintering, despite the high content of cordierite in the initial powder mixture. But they observed that toughness and fracture strength of the obtained composites depend on the weight percent of cordierite present in the initial powder mixture.

In the present study the effect of addition of zirconia (up to 30 wt. %) on the physical, thermal and mechanical properties of the fabricated cordierite-zirconia composites, as well as, their phase composition and microstructure were examined.

## MATERIALS AND METHODS

### Materials

The materials used in this study were pure aluminum tri-isopropoxide (Fluka, Germany), magnesium nitrate hexahydrate (BDH, UK), extra pure tetraethyl orthosilicate, TEOS (Loba chemicals, India) and partially stabilized ZrO<sub>2</sub> powder having mean particle size of 729 nm and specific surface area of 14.19 m<sup>2</sup>/g (TZ-3Y, Tosoh corporation, Japan).

### Composites Preparations

Stoichiometric amounts of Mg (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, aluminum alkoxide and TEOS, equivalent to the Stoichiometric composition of cordierite, were carefully weighed. Firstly, boehmite sol was prepared by hot water hydrolysis of aluminum alkoxide. Excess amount of water [1 (alkoxide):100 (H<sub>2</sub>O)] was added to ensure complete hydrolysis. The temperature was kept constant at 80°C under vigorous stirring for 2 hr. 4 ml of nitric acid was added which lead to a clear sol. Vigorous stirring was continued for another 2 hr at 80°C. Mg (NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O was dissolved in water and added to the transparent sol while stirring. TEOS was hydrolyzed by the addition of excess hot water to TEOS under vigorous stirring at 80° C. nitric acid was used as a catalyst for the hydrolysis to obtain silica sol and then was added to the Al- Mg clear sol and vigorously stirred for 1hr at 80°C.

Additions of ZrO<sub>2</sub> in weight proportions of 10, 20 and 30 wt% were made prior to the final addition of nitric acid (gelation step). Hereafter, these mixtures are denoted CZ<sub>10</sub>, CZ<sub>20</sub> and CZ<sub>30</sub>. Another 5 ml of nitric acid was added to the mixture under gentle stirring until complete gelation.

The gels were dried and calcined at 650° C to burn off the organic and nitrate compounds. Rectangular specimens with dimensions of 15X5X5 mm for mechanical properties were uniaxially pressed at 100 MPa. The samples were fired at 1350° and 1450°C with soaking time of 2 hr at the peak temperature.

### Characterization

Bulk density of the fabricated composites was evaluated using the Archimedes, water displacement method (ASTM C-20). XRD analysis of powdered samples using monochromated Cu K<sub>α</sub> radiation (D 500, Siemens, Mannheim, Germany) was applied to identify crystalline reaction products. Microstructures were examined by SEM (Model XL 30, Philips, Eindhoven, Netherlands). Bending strength was measured using a three point bending test on a universal testing machine (Model 4204, Instron Corp., Danvers, Mass.) at a crosshead speed of 0.5 mm/min and support distance of 40 mm At least 10 specimens were measured for one data point.

## RESULTS AND DISCUSSION

X-ray diffraction patterns of cordierite gel powders heated at different firing temperatures are shown in Fig.1. Synthetic orthorhombic cordierite is the only observed

phase for the specimens heated at 1300°C up to 1400°C. Maximum cordierite content was found to be formed on firing the samples at 1350°C. Dissociation of cordierite was observed on increasing the heating temperature to 1400°C. XRD analysis of the composites fired at 1350°C and 1450°C are shown in Figs.2 & 3. XRD patterns of the bodies fired at 1350°C revealed that the addition of more than 10 wt. % ZrO<sub>2</sub> has resulted in the formation of zircon (tetragonal phase) in the synthetic cordierite matrix. In addition baddeleyite (monoclinic- ZrO<sub>2</sub>) and stabilized tetragonal zirconia were also depicted. Formation of zircon was expected and agrees with the results of Hirvonen et.al<sup>(19)</sup> and Nagarajan & Rao<sup>(20)</sup>. Hirano and Inada<sup>(17)</sup> suggested the following reaction for cordierite-zirconia composite containing 15-35 wt. % ZrO<sub>2</sub>:



It seems that, the possible reaction sequence of the specimens fired at 1350°C could be as follows: in samples CZ<sub>0</sub>, initially μ-cordierite is formed. With increasing the firing temperature spinel and cristobalite react to produce α-cordierite. A small amount of mullite, formed initially, also reacts with spinel to produce α-cordierite. In order to discuss the reactions in CZ<sub>10</sub>, CZ<sub>20</sub> and CZ<sub>30</sub> samples, we have to note that ZrO<sub>2</sub> itself is nearly as basic as Al<sub>2</sub>O<sub>3</sub>; they tend to form solid solutions at high temperatures<sup>(23)</sup>. Further MgO readily reacts with ZrO<sub>2</sub> to form a solid solution<sup>(24)</sup> along with the formation of t-ZrO<sub>2</sub>. At low temperature a reaction between spinel and μ-cordierite and small amounts of mullite is expected. However, mullite is not expected to be retained permanently as a separate phase, because it will continue to react with spinel to produce α-cordierite, which thermodynamically the most stable cordierite phase. Since the temperatures are sufficiently high, reaction between SiO<sub>2</sub> and ZrO<sub>2</sub>, which produces zircon, also occurs. Formation of zircon cuts into the availability of SiO<sub>2</sub> for formation of α-cordierite and gives the suspicion that this may be the reason for the formation of mullite at high temperatures. However, mullite appears at lower temperatures as an independent phase and zircon forms only at higher temperatures. According to Hirvonen et al<sup>(19)</sup> formation of zircon is often assisted by the mullite. It seems that mullite is an intermediate phase which only assists the formation of zircon, but at higher temperature of 1350°C it reacts with spinel to form α-cordierite. The presence of traces of m-zirconia at 1450°C suggests that during reaction between spinel and μ-cordierite, some of MgO is given up from ZrO<sub>2</sub> and hence this MgO-deficient ZrO<sub>2</sub> transforms to the monoclinic phase upon cooling. Nagarajan and Rao<sup>(20)</sup> reported in their study another aspect. They suggested the formation of mullite solid solution in cordierite. Formation of a solid solution in which cordierite structure is preserved would result in significant deficiency in MgO and hence MgO would begin to diffuse in from neighboring t-ZrO<sub>2</sub> grains containing MgO. In our study the presence of mullite at 1450°C does not support such possibility. Mullite was present in all batches fired at 1450°C. It is due to the incongruently melt of Mg-cordierite to mullite and a liquid. The considerable amount of amorphous phase detected in the XRD patterns of the samples fired at 1450°C confirmed the former suggestion. We could not detect cordierite peaks in the XRD patterns of the samples containing ZrO<sub>2</sub> and fired at 1450°C. The lack of cordierite reflex is due to the reaction that occurs between silica and ZrO<sub>2</sub>, which results in the formation of zircon. These results agree with those of Hirvonen et al<sup>(19)</sup> and Sun et al<sup>(25)</sup>. Sapphirine and baddeleyite (m-ZrO<sub>2</sub>) were depicted with a complete absence of t- ZrO<sub>2</sub> in specimens containing ZrO<sub>2</sub> and fired at 1450°C. It seems that when the specimens were sintered at 1450°C, the reaction between cordierite and ZrO<sub>2</sub> particles was severely limited, which is explained by the formation of an Al<sub>2</sub>O<sub>3</sub>- SiO<sub>2</sub>-Y<sub>2</sub>O<sub>3</sub>

intergranular phase acting as a chemical reaction barrier. Destabilization of t- ZrO<sub>2</sub> due to diffusion of Y; through ZrO<sub>2</sub>; into the glassy phase is leading to the transformation to m-symmetry<sup>(26)</sup>.

The density is dependent on sintering temperature and amount of zirconia. Fig. 4 shows that the composite density systematically increased with the content of zirconia in the sintered bodies (note that the theoretical density of cordierite is 2.51 g/cm<sup>3</sup> whereas the density of m-zirconia is 5.85g/cm<sup>3</sup><sup>(1)</sup>). The density of sintered bodies with the same ZrO<sub>2</sub> amount increased with sintering temperature, because of the formation of mullite which recrystallized from the liquid phase (the theoretical density of cordierite is 2.51g/cm<sup>3</sup>, whereas that of mullite is 3.18g/cm<sup>3</sup>).

Figures. 5,6 and 7 showed the microstructure of the fracture, thermally etched surfaces of the specimens sintered at 1350°C. SEM micrograph of the CZ<sub>0</sub> samples showed agglomerations of fine cordierite grains together with well crystalline prismatic cordierite crystals (Fig.5). CZ<sub>30</sub> SEM micrograph (Fig.7) showed some zircon grains crystallized out as a reaction product (the light areas), which is in complete agreement with XRD findings. The microstructure of sample CZ<sub>0</sub> fired at 1450°C showed well-shaped laminar crystals together with clusters of well crystalline cordierite grains (Fig.8). The microstructure of CZ<sub>10</sub> and CZ<sub>20</sub> samples fired at 1450°C is identical showing needle like and leaf like mullite crystals (Fig. 9&10). The presence of very fine ZrO<sub>2</sub> dispersed in the amorphous phase is detected in Fig. 10.

Three point bending strength results of the bodies fired at 1350°C are shown in Table 1. It shows that the addition of ZrO<sub>2</sub> up to 10 wt% results in a significant increase in the bodies bending strength. On the other hand, addition of ZrO<sub>2</sub> higher than 10 wt% results in a decrease in the bending strength. It is noticed that specimen containing 30 wt% ZrO<sub>2</sub> shows a large reduction in the bending strength. It is well known that bending strength is related to the microstructure of the composites. Figs.6 and 7 show the scanning electron micrographs of the fracture surfaces of composites containing 10 and 30 wt% ZrO<sub>2</sub>, respectively. Fig.6 (CZ<sub>10</sub>) shows a homogeneous dispersion of zirconia inclusions in the cordierite matrix in comparison to Fig.7 (CZ<sub>30</sub>), which shows the existence of ZrO<sub>2</sub> agglomerates. The homogeneous distribution of the ZrO<sub>2</sub> particles in the cordierite matrix is expected to enhance the bodies bending strength. While, the reduction in bending strength of the specimens containing 30 wt% ZrO<sub>2</sub> is due to the heterogeneous dispersion of zirconia inclusions. Specimens fired at 1450°C show an increase in the bending strength values. The strength dependency could not be correlated to any specific strengthening mechanism prevailing in cordierite matrix because of the extensive phase changes taking place at this sintering temperature and to the presence of various phases in the sintered samples. Travitzky and Claussen<sup>(26)</sup> stated that multiphase composites consisting predominantly of spinel, and zircon with both intra- and intergranular m-zirconia particles, exhibit strength values higher than that of the respective single phase. We believe that the development of the mullite grains in a textured structure (Fig.12) have a beneficial effect on the composites mechanical properties.

## CONCLUSIONS

- 1- Cordierite was easily obtained by sol-gel route and examined both in its pure form and in a composite with 10, 20 and 30 wt % ZrO<sub>2</sub>.

- 2- The bulk density of all composites increased with temperature.
- 3- Due to t-ZrO<sub>2</sub> loss of Y (on firing at 1450°C) it increasingly destabilized leading to the transformation to the m-symmetry.
- 4- The increase of the firing temperature of the cordierite/zirconia composites to 1450°C improved their mechanical properties due to the formation of the textured mullite.

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Table 1: Three point bending strength of the cordierite – zirconia composites fired at 1350°C and 1450°C.

Symbol	Three point bending strength, (Mpa)	
	1350°C	1450°C
<b>CZ<sub>0</sub></b>	194.88	243.52
<b>CZ<sub>10</sub></b>	275.22	526.27
<b>CZ<sub>20</sub></b>	102.04	531.15
<b>CZ<sub>30</sub></b>	95.67	647.042

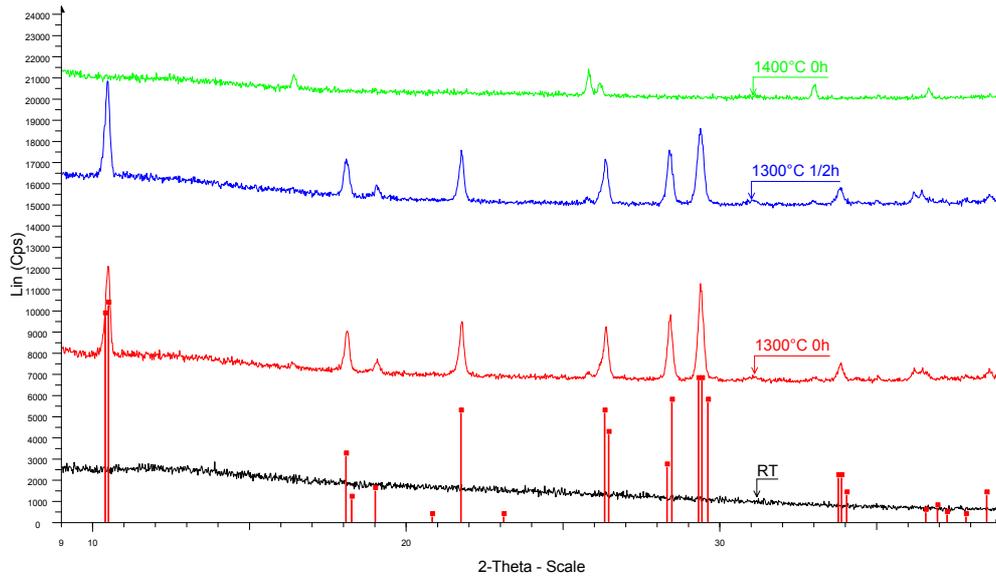


Fig. 1: High temperature XRD patterns of the cordierite gel

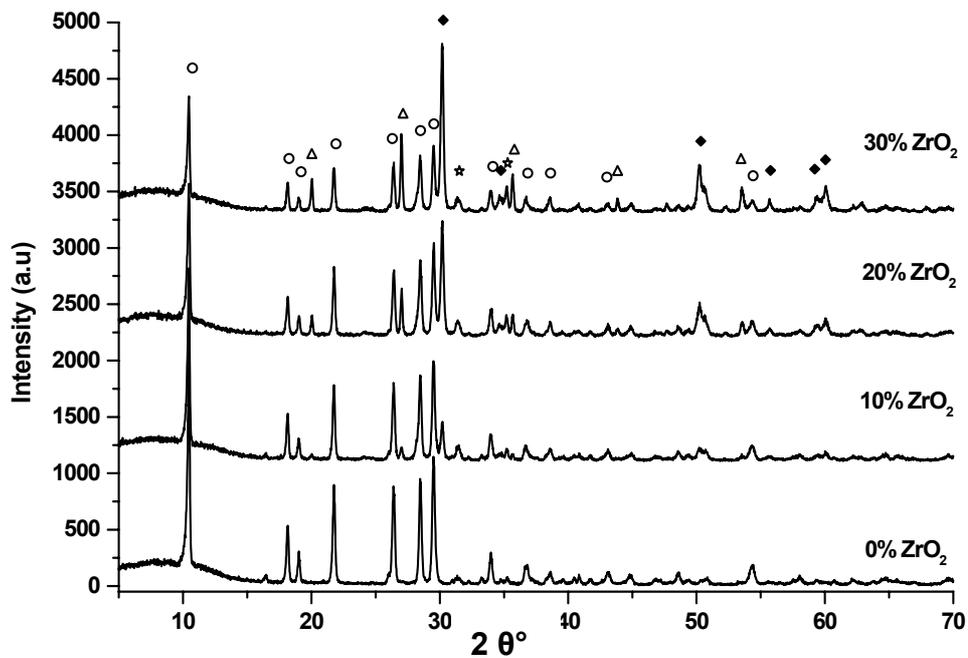


Fig. 2: XRD patterns of cordierite zirconia composites fired at 1350°C

♦ = t-ZrO<sub>2</sub>, ★ = m-ZrO<sub>2</sub>, Δ = Zircon, ○ = Cordierite

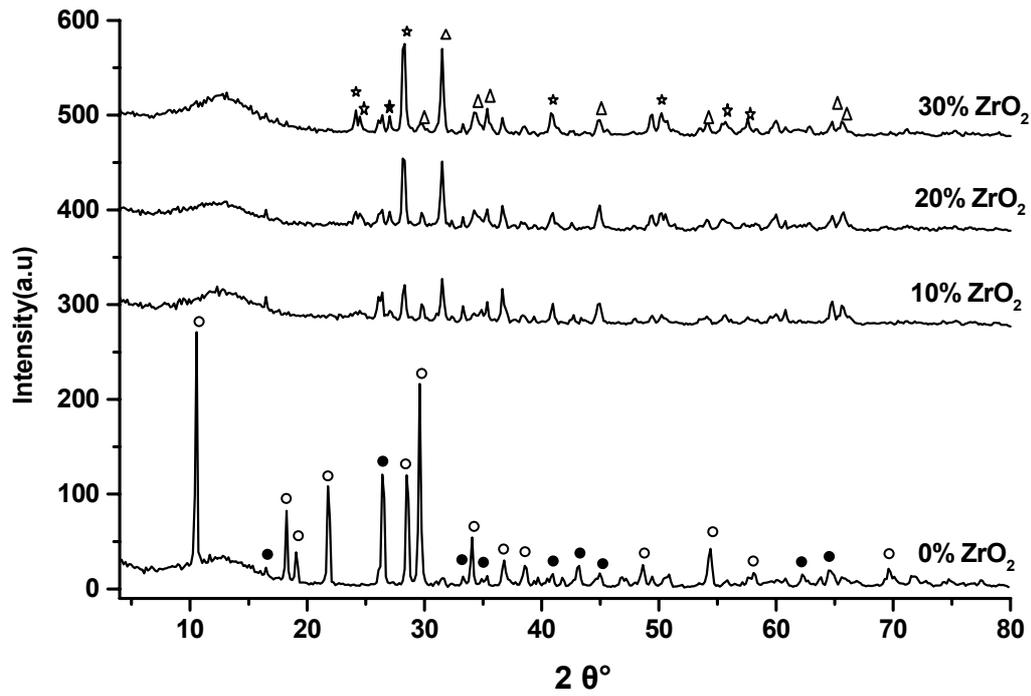


Fig. 3: XRD patterns of cordierite zirconia composites fired at 1450°C  
 ☆= m- ZrO<sub>2</sub>, ★ =Zircon, Δ =Sapphirine, ● =Mullite and ○ =Cordierite

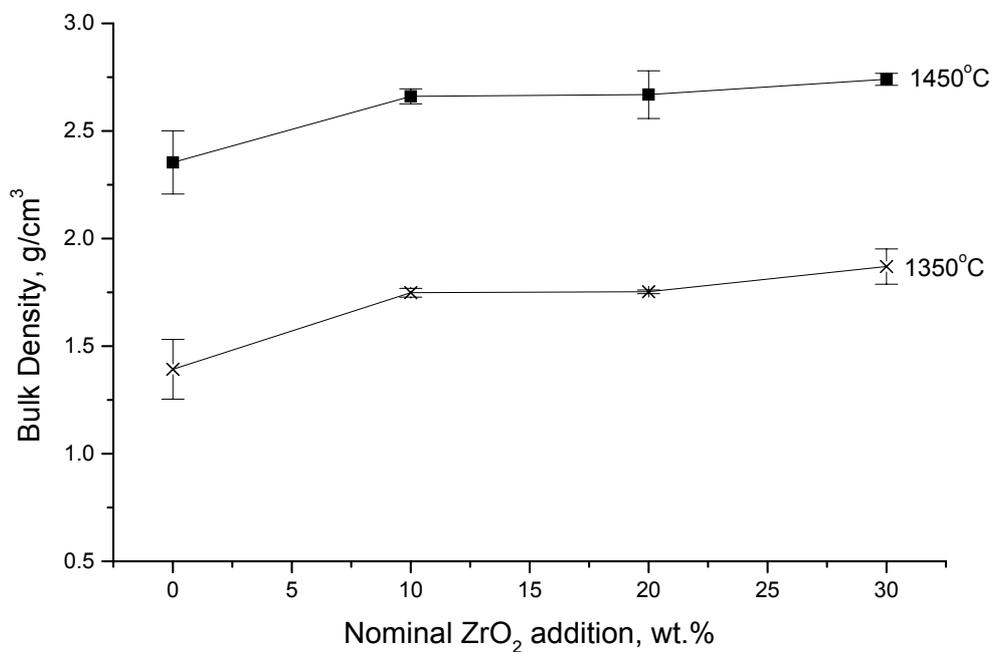


Fig.4 Bulk density of different batches fired at 1350°C and 1450°C.

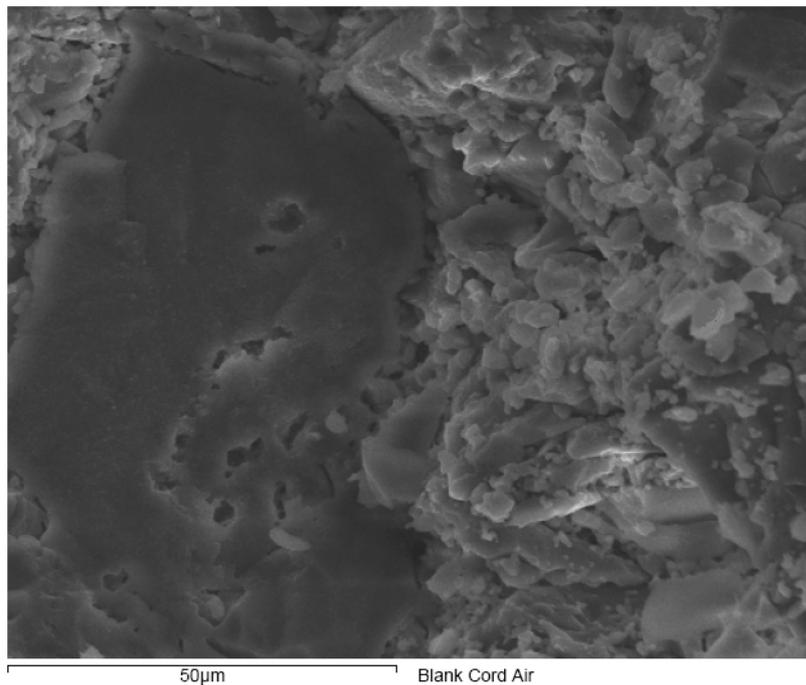


Fig.5 SEM micrograph of the CZ<sub>0</sub> fired at 1350°C.

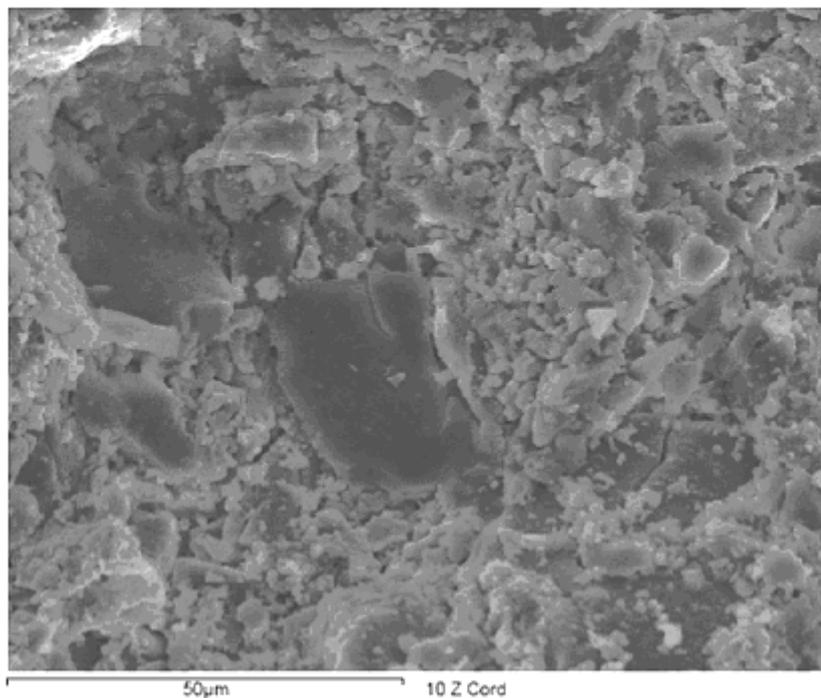


Fig.6 SEM micrograph of the CZ<sub>10</sub> fired at 1350°C.

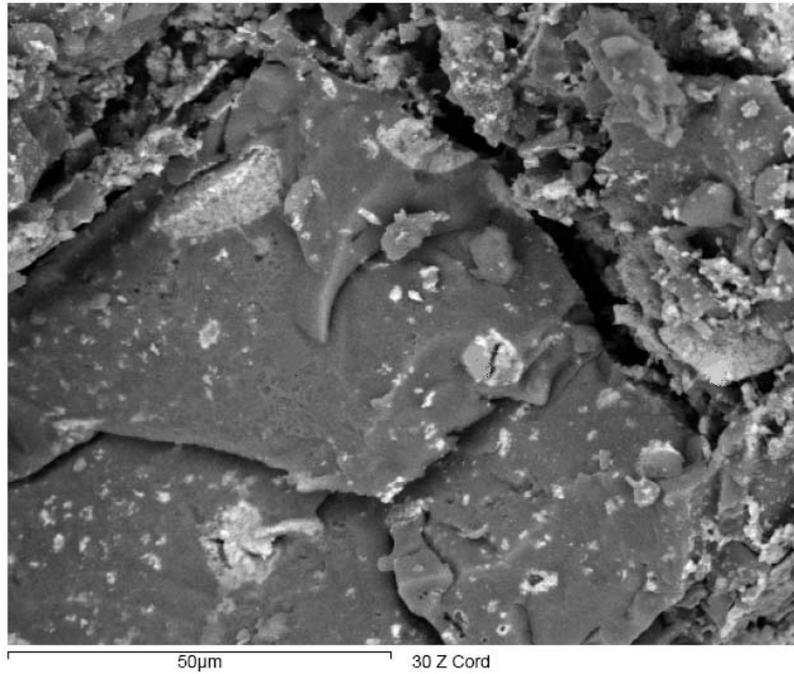


Fig. 7 SEM micrograph of the CZ<sub>30</sub> fired at 1350°C. Fine cordierite grains occurring in batches with zircon grains on its surface.

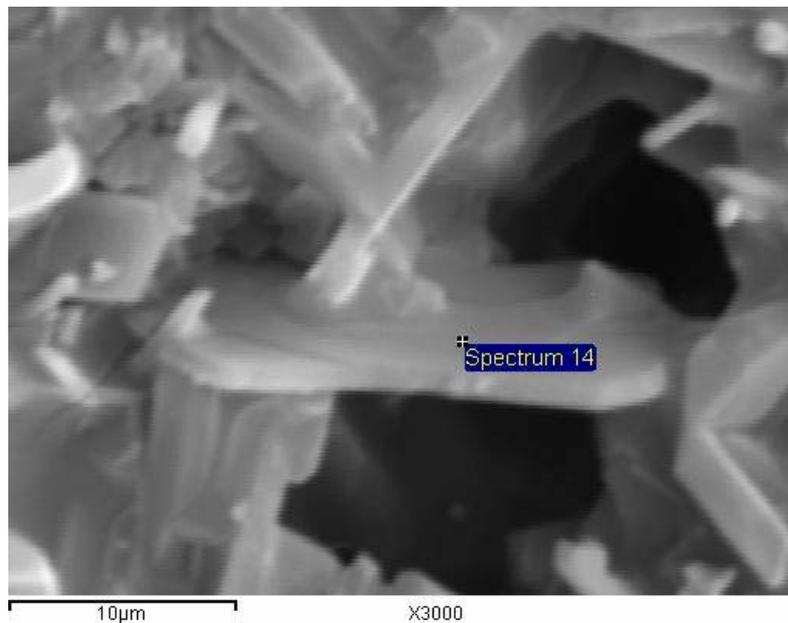


Fig.8 SEM micrograph of the CZ<sub>0</sub> fired at 1450°C. Prismatic well developed crystalline cordierite, uniform in size with different orientation.

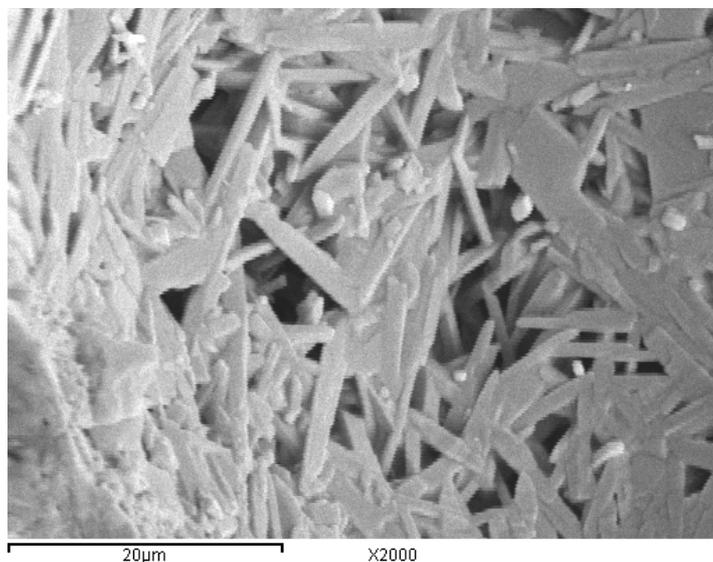


Fig.9. SEM micrograph of CZ<sub>10</sub> sample fired at 1450°C showing needle like mullite crystals.

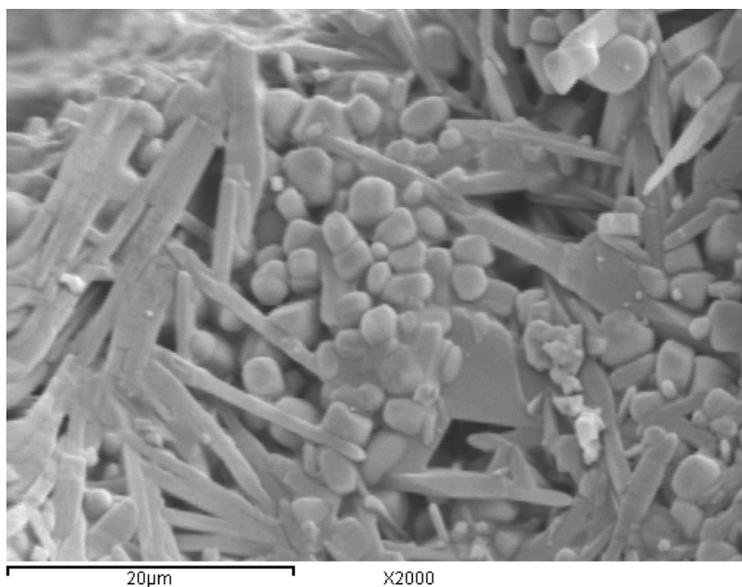


Fig.10. SEM micrograph of CZ<sub>20</sub> sample fired at 1450°C showing leaf like mullite crystals

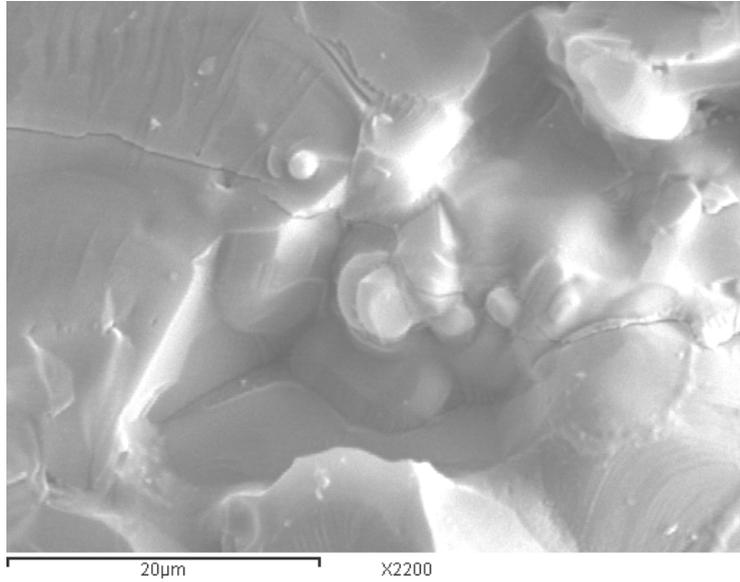


Fig.11. CZ<sub>20</sub> SEM micrograph showing amorphous phase with embedded zirconia grains. Samples fired at 1450°C.

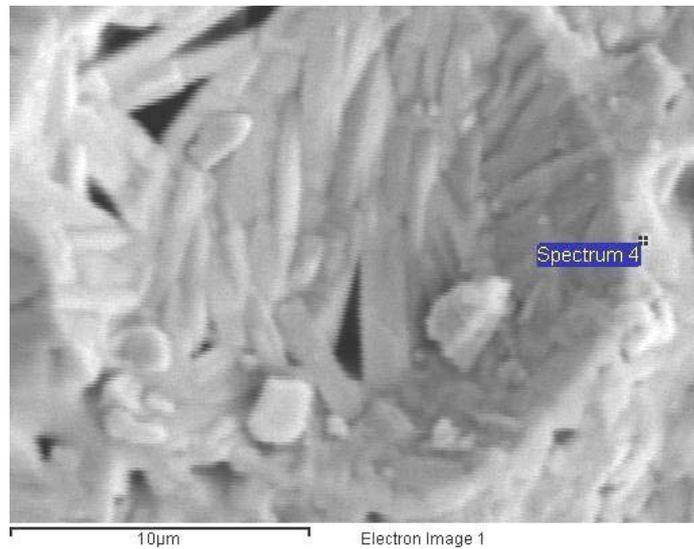


Fig.12 SEM micrograph showing textured mullite developed in cordierite/zirconia composite (CZ<sub>10</sub>) fired at 1450°C.