



## Effect of $ZrO_2$ on the reaction sintering of $MgO-Al_2O_3-SiO_2$ system in the Cordierite composition

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### ABSTRACT

Present investigation was undertaken to synthesis and characterize pure cordierite and cordierite- $ZrO_2$  composite by sol-gel technique from dehydroxylated kaolinite, precipitated silica and  $Mg(NO_3)_2$  in presence of  $ZrO_2$ . The gels are dried and sintered at different temperatures ranging from 1200 to 1350°C. Magnitude of sintering was determine by measuring some fired characteristics including shrinkage, apparent porosity and true density. The evolution of crystalline phases and the microstructures have been studied using X-ray diffractometry and scanning electron microscopy. The results obtained clearly demonstrate that the mechanical properties and the microstructure were critically dependent on the  $ZrO_2$  content and the retained porosity.

**KEYWORDS :** Cordierite, Zirconia, Composites, Flexural strength, XRD

### Introduction

The study of cordierite ceramics synthesis and its application was a subject of many papers after C.W. Parmelee and G.H. Baldwin showed that in the system clay-feldspar-talc, ceramic masses with good thermal and electric properties could be obtained [1–5]. 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. The industrial production of cordierite ceramics makes use of fireclays, technical alumina, and natural magnesia materials such as magnesite, dunite, and talc. Analysis of literature data on cordierite [6–8] shows that in the production of cordierite ceramics based on fireclays and magnesia materials the cordierite is synthesized mainly through spinel, and also through mullite. 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 gels [9,10]. 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 purpose of the present study was to develop a body of cordierite composition from dehydroxylated clay through semi colloidal route and to incorporate  $ZrO_2$  for enlargement of the softening range and improvement of the thermo-mechanical properties.

### Experimental

For this purpose Rajmahal china clay of Indian origin was selected. This was dehydrated at 600°C to 650°C for a soaking period of two hours. For the actual synthesis of the precursor powder requisite amount of calcined caly and dried precipitated silicawas mixed and dispersed in a calculated volume of 0.1 molar  $Mg(NO_3)_2$  solution according to cordierite composition.  $Mg(OH)_2$  gel formation was carried out by the addition of ammonia at controlled pH. The enblock gel contained the clay particles as suspended in the matrix. The mixed gel was processed to remove the adhering soluble impurities, dried, ground and milled to fine sate of subdivision. The precursor powder was characterized by some physico-chemical testings. Four different batches were prepared with gradual addition of  $ZrO_2$  in the form hydroxide with the precursor powder. The proportion of  $ZrO_2$  were 5, 10 and 15% w/w respectively. Before fabrication the precursor powder was calcined at 900°C in order to remove the loosely bound gel water as otherwise this will lead to high shrinkage causing serious faults. 10% unclined precursor powder was used as bond. Rectangular bars were fabricated by applying uniaxial pressure of 10.80 kg/cm<sup>2</sup> in steel moulds. Before firing they were thoroughly died at 120°C. The pressed compacts were subjected to sintering at temperatures at 1200, 1250, 1300 and 1350°C respectively. Because of the small firing range of the cordierite body the soaking time was controlled at 1 hour.

The magnitude of sintering was examined in relation to  $ZrO_2$  content through determination of some fired characterized including linear shrinkage, apparent porosity, and true density. Spalling resistance of the sintered composite is one of the important characteristics upon

which the application depends. This was done by heating and followed by air quenching. The cycle was repeated for ten times.

The development of crystalline phases was ascertained by XRD analysis (Philips PW 1790 x-ray diffractometer). Finally the microstructural analysis was carried out on the fractured surface by using model S-530. HITACHI, Tokyo, Japan.

### Results & Discussion

Precursor powder of  $MgO-Al_2O_3-SiO_2$  system of cordierite composition was synthesized by utilizing commonly available china clay. After dehydroxylation which generally occurs within the temperature range 450-650°C the clay structure is completely destroyed with the generation of active  $SiO_2$  and  $Al_2O_3$ . Thus for enhancing the rate of solid state reactions of clays with other oxide constituents the only way to increase the reactivity is the dehydroxylation process.

Chemical analysis of the clay indicated pure kaolinitic nature with minimum impurities (Table-I).

Constituents	Percentage present in	
	Raw China clay	Dehydroxylated China clay
$SiO_2$	48.30	55.53
$Al_2O_3$	37.75	42.53
$Fe_2O_3$	0.55	0.63
CaO	0.10	0.12
LOI	18.05	---

**Table – I: Chemical analysis of experimental china clay**

After dehydration the percentage of  $SiO_2$  and  $Al_2O_3$  correspondingly increased with no loss on ignition.

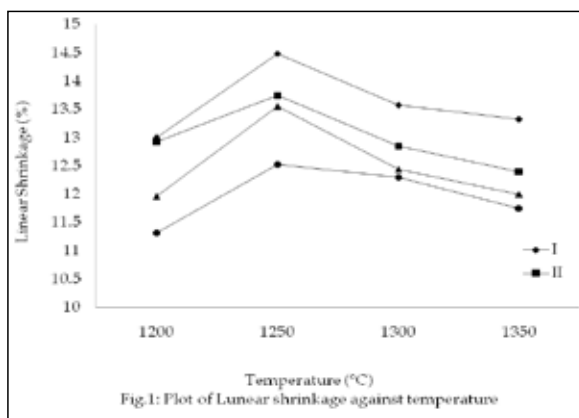
The important physico-chemical characteristics of synthesized precursor powder are given below:

Properties	Values
Chemical analysis	
$SiO_2$	43.30
$Al_2O_3$	29.69
MgO	11.64
LOI	14.95
Molar Ratio $MgO:Al_2O_3:SiO_2$	2:2:5
DTA peaks	390°C (Endothermic) 950°C (Exothermic)
Specific Surface area (m <sup>2</sup> /gm)	125
Loose Bulk density (gm/cc)	0.351

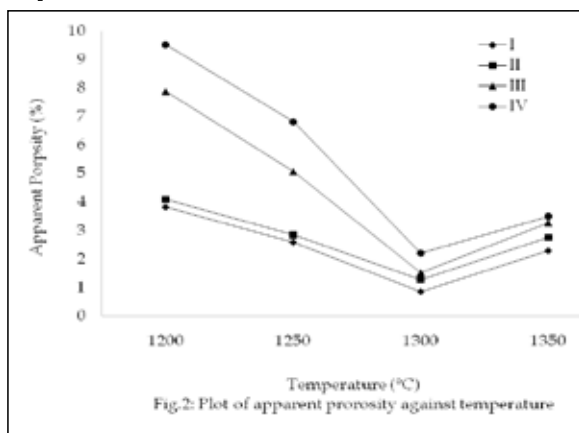
**Table – II: Physico-chemical characteristics of synthesized precursor powder**

The texture of the precursor powder was fine and optically homogeneous. Loose bulk density (Table-I) ascertained minimum agglomeration and reactivity of the precursor. The rate of reaction as well as densification depends on the point of contact between the grains. Differential thermal analysis indicated two peaks one endothermic at 390°C and another small exothermic at 950°C. The endothermic peak was associated with the expulsion of hydroxyl water from Mg(OH)<sub>2</sub> gel. The exothermic peak might be due to formation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> from dehydroxylated clay prior to mullite formation.

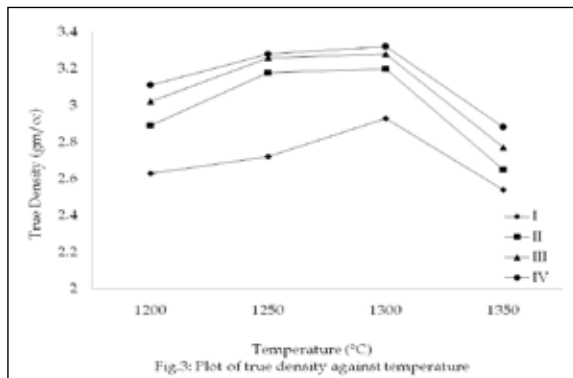
The magnitude of densification was manifested through shrinkage of the fabricated shapes caused by various solid state reactions, formation of liquid, etc. this shrinkage in the triaxial body was mainly due to high temperature reactions leading to cordierite formation as the bodies were fabricated using the calcined mixture. Variation of shrinkage is not of high order; it is from about 8 to 12%. With the incorporation of ZrO<sub>2</sub>, shrinkage decreased due to lower amount of liquid formation. The shrinkage temperature curves (Fig. 1) were nonlinear in nature. It increase up to 1250°C following which it decreases slowly which might be associated with the orientation of the formed cordierite in the matrix.



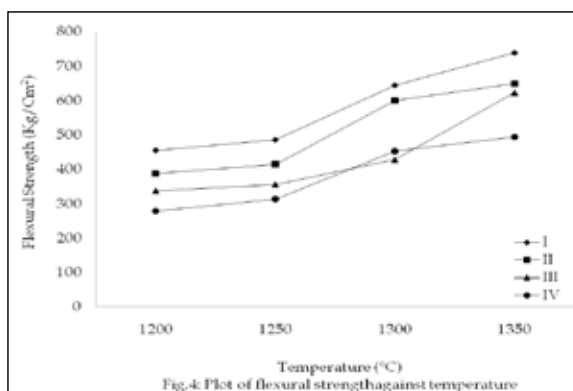
As the sintering proceeded through the decrease in free energy particle migration occurred through the formation of thermodynamically more stable phase which was cordierite in this case. The general trend was porosity decreased with temperature. The low porosity values indicates that densification increased with cordierite formation, with increase in ZrO<sub>2</sub> content porosity increased due to more refractory nature of the ZrO<sub>2</sub> containing phases (Fig. 2). Thus ZrO<sub>2</sub> addition does not influence the mechanism of reaction on firing. Incorporation of ZrO<sub>2</sub> modifies the matrix condition.



Change of true density in a fired body is related to the nature of phase transformation taking place. In the present investigation true density is directly proportional to the ZrO<sub>2</sub> content in the composition. The temperature relationship has been represented in Fig. 3 where density increased up to 1250°C and then decreased at 1350°C due to dissolution of high density phases.



The mechanical strength of a composite body is usually related to the nature of the phases as well as on the evolved microstructure. The flexural strength is significantly high and it is decreased with incorporation of ZrO<sub>2</sub>. In each case maximum strength is achieved at 1350°C and Batch-I i.e. without ZrO<sub>2</sub> exhibit the highest value. With ZrO<sub>2</sub> incorporation the value gradually decreases might be due to phase separation in the matrix (Fig. 4).



Rapid fluctuation of temperature usually generates stresses in a composite body depending on the microstructure and that is related to the phase transformation and the nature of the glassy phase at the grain boundary. After offering the thermal shock there is reduction in strength but that is not of high order. The reduction of mechanical strength was significantly noticed with batch-IV. The batch composition without ZrO<sub>2</sub> exhibits maximum retention of strength at 1350°C, which might be due to proper interlocking of the crystals.

In order to study the compositional effect on the generation of crystalline phases of the reaction sintered products X-ray diffraction analysis was performed with 1350°C fired samples. In each sample formation of cordierite phase is identified as desired from the chemical nature of the precursor powder along with mullite as major phase. The incorporated ZrO<sub>2</sub> is found to be retaining in tetragonal form. The t-ZrO<sub>2</sub> phase in the matrix is responsible for offering greater mechanical strength and toughness to such body. Again the presence of mullite phase contributes to higher thermal shock resistance.

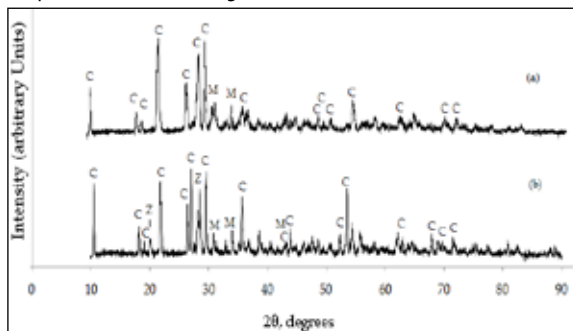
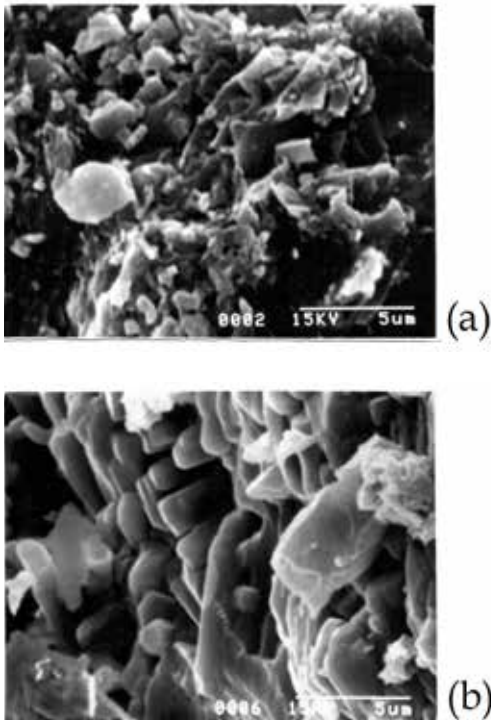


Fig. 5: X-Ray Diffraction pattern of sample fired at 1350°C. (a) Batch-I and (b) Batch-III

Thus the incorporation of  $ZrO_2$  in the cordierite matrix improves the thermal shock resistance as evident from the values of residual strength after spalling.

The assessment of the phase assemblage in the microstructure was studied through scanning electron microscopy with the samples fired at  $1350^\circ C$ . Cordierite microstructure without  $ZrO_2$  addition indicates existence of glassy phase which diminishes with the addition of  $ZrO_2$ . With addition of 5%  $ZrO_2$  the cordierite grains turned into rounded or sub-rounded shape and distributes homogeneously into a compact mass and grain boundary was sharp.  $ZrO_2$  grains (brighter ones) were smaller and dispersed both in inter and intra-granular positions. It is interesting to note that there was a transangular crack in the interface. This might be due to some lattice strain developed due to change in the glass composition. But with the increase in  $ZrO_2$  content this was not visible.



**Fig. 5: Scanning Electron Microscopy of sample fired at  $1350^\circ C$ . (a) Batch-I and (b) Batch-III**

$ZrO_2$  incorporation increases the grain growth. The microstructure changed to elongated cordierite grain properly interlocked with rounded  $ZrO_2$  particles and this was found to be responsible for enhance mechanical strength. The retention of t-  $ZrO_2$  induced the change of morphology of cordierite grains.

### Conclusion

Cordierite- $ZrO_2$  composite prepared by sol-gel technique from dehydroxylated kaolinite, precipitated silica and  $Mg(NO_3)_2$  in presence of  $ZrO_2$ , offer very good properties in both enhancing the sinterability and mechanical properties of cordierite. Cordierite- $ZrO_2$  body can successfully prepared by using about 10%  $ZrO_2$ . Flexural strength of the composites was degraded by increasing the  $ZrO_2$  content. This is due to increase in residual porosity and phase separation in the matrix. The incorporated  $ZrO_2$  is found to be retaining in tetragonal form. The t- $ZrO_2$  phase in the matrix is responsible for offering greater mechanical strength and toughness to such body.

### Reference

1. Parmelee G.W. and Baldwin G.H. (1913). Anwendung von Talk in Porzellanmassen. Trans. Am. Soc., 15, 606.
2. Morrell R. (1979). The mineralogy and properties of sintered cordierite glass-ceramics, Proc. Br. Ceram. Soc., 28, 53–71.
3. Das K., Das S.K., Mukherjee B. and Banerjee G. (1998). Microstructural and mechanical properties of reaction-sintered mullite-zirconia composites with magnesia as additive.

Interceram. 47 (5), 304–312.

4. Travitzky N.A. and Claussen N. (1989). Chemical stability of cordierite- $ZrO_2$  composites. J. Eur. Ceram. Soc., 5, 327–331.
5. Das Gupta A., Sen P.S., M.K., Sinha and Basu M.K. (1994). Effect of  $ZrO_2$  addition on strength and dilatation behaviour of cordierite ceramics. J. Mater. Sci. Lett. 13, 332–334.
6. Grosjean P. (1995). Chlorite and chlorite-rich talcs in cordierite, Interceram. 44 (6) 411–414.
7. Nakahara M., Kondo Y. and Hamano K. (1999). Effect of particle size of powders ground by ball milling on densification of cordierite ceramics, J. Ceram. Soc. Japan 107 (4), 308–312.
8. Lim B. and Jang H.M. (1993). Homogeneous fabrication and densification of cordierite-zirconia composites by a mixed colloidal processing route. J. Am. Ceram. Soc. 76 (6), 1482–1490.
9. Semar W., Pannhorst W., Hare T.M. and Palmour III H. (1989). Sintering of a crystalline cordierite/ $ZrO_2$  composite, Glstech. Ber. 62 (2), 74–78.
10. Genevriev M. and Mocellin A. (1996). Reaction sintering and mechanical behavior of cordierite containing sapphirine dispersoids. J. Am. Ceram. Soc. 79 (8), 2098–2104.