

## Preparation and Thermal Evolution of the Microstructure of Sol–Gel-Derived Cordierite and Cordierite–Zirconia Powders\*

V. S. NAGARAJAN AND K. J. RAO†

*Materials Research Centre, Indian Institute of Science,  
Bangalore 560 012, India*

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Pure cordierite and a cordierite–ZrO<sub>2</sub> (20 wt%) composite have been prepared by the sol–gel technique using both acid and base catalysts. The evolution of crystalline phases and the microstructures have been studied using X-ray diffractometry, IR spectroscopy, and transmission electron microscopy. The effect of acid/base catalysis on the nature of the reaction has been carefully examined. Formation of observed products have been rationalized keeping in view the various acid–base reactions between the oxides and the catalyst in the sol. The molecular electronegativity differences of the component oxides have been used to understand the observed reactions. In all cases, the formation of  $\alpha$ -cordierite has been observed at temperatures >1200°C only. Zircon is formed in the composites and ZrO<sub>2</sub> is mostly present as particulates with c/t structure. Evidence has been found for the possible solid solution formation of cordierite and mullite. ZrO<sub>2</sub> has been stabilized in the c/t phase by reaction with MgO, but at higher temperatures the exsolution of MgO from ZrO<sub>2</sub> has been evidenced through microscopic studies. © 1991 Academic Press, Inc.

### Introduction

Cordierite (2MgO·2Al<sub>2</sub>O<sub>3</sub>·5SiO<sub>2</sub>) is a technologically important ceramic, particularly as a low thermal expansivity material of good chemical stability. It possesses a low dielectric constant which has opened new dimensions for its use in electronic packaging (1–4). Recently there have been reports of the preparation of ZrO<sub>2</sub>–cordierite composite ceramics (5, 6) and notably ZrO<sub>2</sub> has been introduced as an exsolution phase from a glassy matrix having a cordierite composition (7–9).

We have examined the possibility of using

ZrO<sub>2</sub> as a toughening phase in many ceramic systems such as aluminosilicates and apatites (10–12). We have found that the sol–gel route is particularly facile to introduce fine particulates of ZrO<sub>2</sub> which are stabilized in their (c/t) phases either initially or at ceramizing temperatures. In apatite composites, ZrO<sub>2</sub> has been found to give rise to a significant improvement of the fracture toughness ( $K_{IC}$ ). Cordierite–ZrO<sub>2</sub> composite is therefore a particularly attractive system to prepare by the sol–gel (13, 14) route and to examine the evolution of cordierite and related structures during heating to the required ceramization temperatures.

In this communication, we report the gel-route preparation of pure cordierite using two different procedures together with prep-

\*Contribution 166.

†To whom correspondence should be addressed.

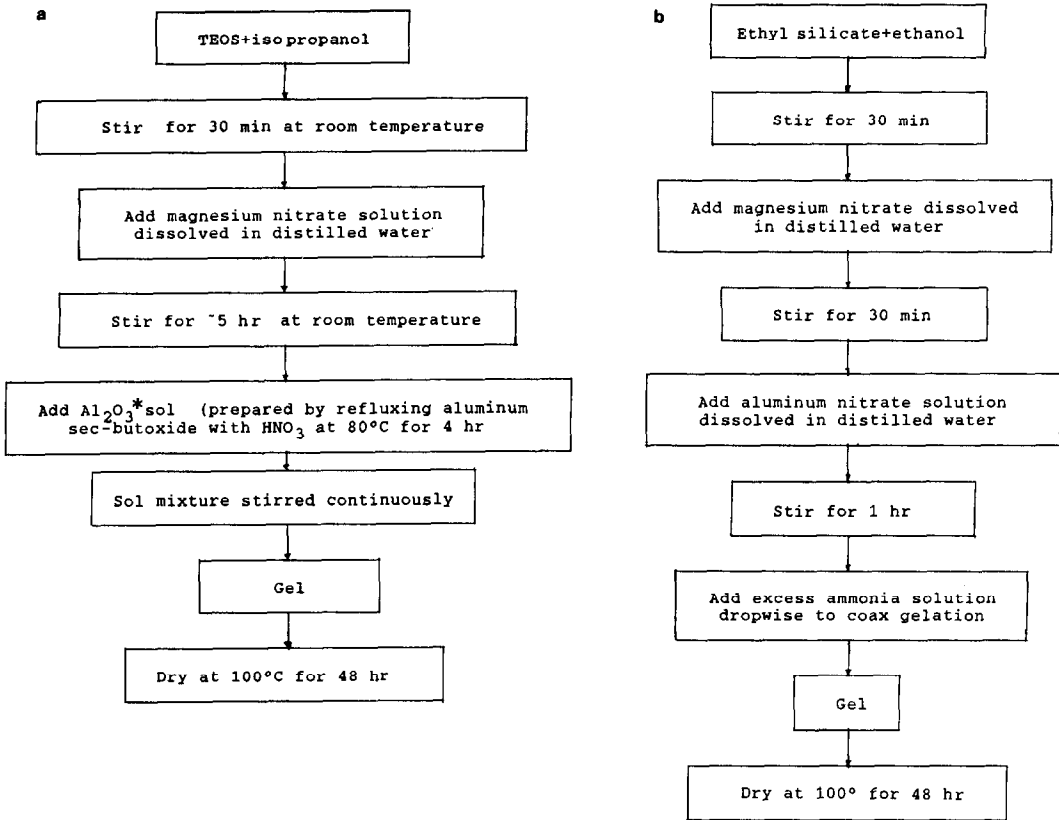


FIG. 1. Preparative procedure for the (a) PC/A and CZ 20/A gels and (b) PC/B gel. \*Add  $ZrO_2$  sol for CZ 20/A gel.

aration of a composite containing  $ZrO_2$  up to 20 wt% by one of the procedures. We have found that while in pure cordierites, mullite ( $3Al_2O_3 \cdot 2SiO_2$ ) and spinel ( $MgO \cdot Al_2O_3$ ) can be residual phases, in  $ZrO_2$ -cordierite composite zircon appears as the only additional phase other than cordierite and  $ZrO_2$ .

### Experimental

Pure cordierite gels were prepared by two routes. In the first method tetraethoxyorthosilane (TEOS) (high purity; Fluka, Germany), aluminum secondary butoxide (high purity; Fluka, Germany), and magnesium nitrate (purity >99%; Loba Chem. India) were used as starting materials and the gel

is designated as acid-catalyzed gel, PC/A. In the second method ethyl silicate (Mettur Chemicals, India), aluminum nitrate, and magnesium nitrate (purity >99%, Loba Chem, India) were used as the starting materials. The resulting gel is designated as base-catalyzed gel, PC/B, because ammonia was used as a catalyst to coax the gelation. The cordierite-20 wt%  $ZrO_2$  gel was prepared from TEOS, aluminum secondary butoxide, zirconium propoxide (high purity; Fluka, Germany), and magnesium nitrate and again the gel is designated as acid-catalyzed, CZ 20/A. The preparative procedures for acid-catalyzed PC/A and CZ 20/A and base-catalyzed PC/B are as shown in Figs. 1a and 1b, respectively. The gels were obtained from clear sol mixtures and calcined at

400°C for 12 hr after drying at 100°C for 48 hr. Fine powders were obtained by crushing in an agate mortar and pestle; no hard agglomerates were noticed. Gel powders were all heated at a rate of 10°/min to temperatures ranging from 800 to 1400°C and held for 2 hr at the desired temperature following which they were air quenched. Powder X-ray diffraction (JEOL, JDX-8P, Japan) was used to identify the various phases present. The most prominent reflection of  $\mu$ -cordierite (101),  $\alpha$ -cordierite (100), spinel (311), cubic/tetragonal ZrO<sub>2</sub> (111), monoclinic ZrO<sub>2</sub> (111 and 11 $\bar{1}$ ), zircon (200), and mullite (210) were used for the identification of phases. The microstructures were characterized using a high resolution transmission electron microscope (HRTEM, JEOL 200 CX, Japan). The infrared spectra were recorded in KBr pellets on a Perkin-Elmer 580 double beam spectrometer.

## Results and Discussion

The stable phase of cordierite is known to be the  $\alpha$ -cordierite in most of the ceramic

preparations. It has hexagonal crystal structure (space group  $D_{6h}^{2}-P6/mmc$ ). The other phases in the MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> system which are of interest to this work are mullite (3Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub>), spinel (MgO · Al<sub>2</sub>O<sub>3</sub>), and forsterite (2MgO · SiO<sub>2</sub>). In the system in which ZrO<sub>2</sub> is present, namely, MgO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-ZrO<sub>2</sub>, the only other phase of interest is zircon (ZrO<sub>2</sub> · SiO<sub>2</sub>). It is interesting that we never observed any of the other possible binaries in all our investigations. Except for ZrO<sub>2</sub> the other oxide unaries are also not present. Indeed, we suspect that ZrO<sub>2</sub> is also present as MgO-stabilized solid solution. We discuss below the thermal evolution of structures in the three preparations PC/A, PC/B, and C20/A.

## Evolution of Crystalline Phases: Pure Cordierite, PC/A, and PC/B

The nature of phases observed in X-ray diffraction studies of PC/A and PC/B heated to various temperatures are summarized in Table I. PC/A is considered an acid-catalyzed gel because prior to gelation alu-

TABLE I  
SUMMARY OF XRD STUDIES<sup>a</sup> IN PURE CORDIERITE AND ZrO<sub>2</sub>-CORDIERITE GELS DURING HEAT TREATMENT

Sample	Temperature of heat treatment (°C)					
	600	800	1000	1200	1300	1400
Pure cordierite (PC/A)	a	a	S $\mu$	$\mu$ M S	C M<< S	C M<< S
Pure cordierite (PC/B)	a	a	$\mu$ S X	$\mu$ S X	C X S<<<	C S<<< X<<<
ZrO <sub>2</sub> -cordierite 20/80 wt% (CZ 20/A)	a	c/t	c/t S $\mu$	c/t $\mu$ S m	C t+m Z M	C Z t+m —

Note. a, amorphous; S, spinel;  $\mu$ ,  $\mu$ -cordierite; M, mullite; X, cristobalite; c/t, metastable cubic/tetragonal; t, tetragonal; m, monoclinic; Z, zircon; C,  $\alpha$ -cordierite.

<sup>a</sup> The phases present are indicated in order of decreasing abundance.

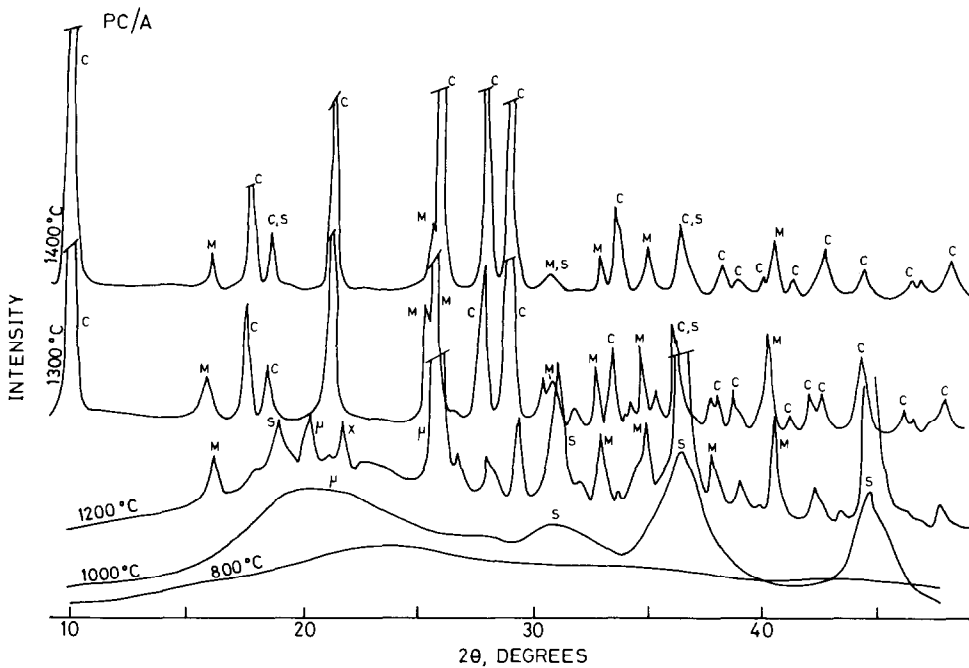


FIG. 2. XRD pattern of PC/A gel heat treated at different temperatures (C,  $\alpha$ -cordierite; M, mullite; S, spinel; X, cristobalite;  $\mu$ ,  $\mu$ -cordierite).

minimum secondary butoxide which was hydrolyzed in dilute  $\text{HNO}_3$ , was added to a mixture of partially hydrolyzed TEOS and magnesium nitrate. PC/B however was hydrolyzed using ammonia and hence may be considered as base catalyzed. X-ray diffraction patterns at various temperatures for PC/A and PC/B preparations are shown in Figs. 2 and 3, respectively. Both PC/A and PC/B remain amorphous till  $800^\circ\text{C}$  and both produce spinel and  $\text{SiO}_2$  (in PC/A as  $\mu$ -cordierite, in PC/B as cristobalite) as initial products of crystallization. The acid-catalyzed PC/A at  $1200^\circ\text{C}$  shows the formation of mullite, a product that is not found even at  $1400^\circ\text{C}$  in the base-catalyzed gel.  $\alpha$ -Cordierite however begins to form only above  $1300^\circ\text{C}$ . In both the acid- and the base-catalyzed gel samples, spinel disappears above  $1300^\circ\text{C}$ , evidently by reaction with  $\text{SiO}_2$ . We recognize that in our acid-catalyzed gel the

medium was not very acidic although in base-catalyzed gel it has been quite sufficiently basic. In order to understand the nature of products formed in acid- and base-catalyzed situations we first designate the component oxides as follows.  $\text{MgO}$  is the most basic and designated as  $b_1$ ,  $\text{Al}_2\text{O}_3$  is amphoteric (both acidic and basic) and designated as  $b_2$  and  $a_2$  and  $\text{SiO}_2$  is acidic, designated as  $a_3$ . The acid and base added as catalysts are designated as A and B. As we have argued elsewhere (11), in PC/A the structure of the gel is conditioned such that the acidic  $\text{SiO}_2$  phase is spatially segregated while the basic  $\text{MgO}$  and  $\text{Al}_2\text{O}_3$  form similarly segregated regions which may be designated  $b_1A$ ,  $b_2A$ , and  $b_1b_2A$ . These are ultra-micro segregations and are not of dimensions which cause turbidity in the sols or gels. At higher temperature the acids are eliminated and evidently the high tempera-

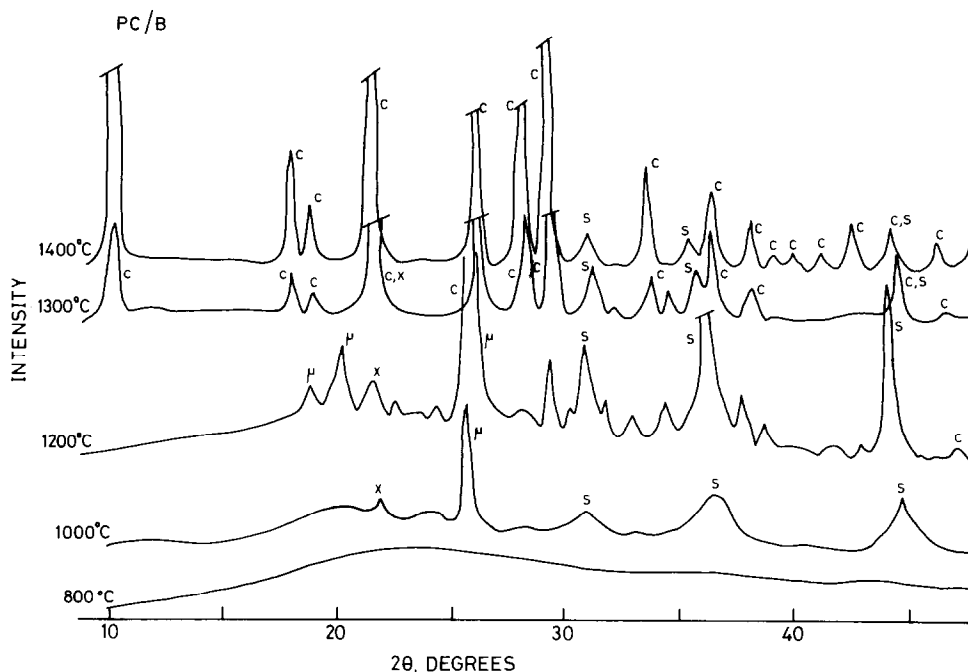


FIG. 3. XRD pattern of PC/B gel heat treated at different temperatures (C,  $\alpha$ -cordierite; S, spinel;  $\mu$ ,  $\mu$ -cordierite; X, cristobalite).

ture reaction in  $b_1b_2A$  leads to the formation of spinel.  $b_2A$  with  $\text{SiO}_2$  would begin to form mullite at high temperatures.  $\text{MgO}$ , being sufficiently ionic, would tend to react readily with  $\text{Al}_2\text{O}_3$  and is therefore unlikely to be found either as an independent phase or as magnesium silicate. Also, the kinetic barrier for the formation of magnesium silicate would be prohibitively high; Si-O covalent bonds have to be excited in order to enable the reaction. However, since  $\text{Al}_2\text{O}_3$  would be present in  $b_1A$  in the gels it reacts at higher temperature with  $\text{SiO}_2$  to form mullite. We may recall here that  $\text{Al}_2\text{O}_3$  is amphoteric and in acid-catalyzed reaction some of it could be considered as being present along with  $\text{SiO}_2$  itself in segregated regions of the gel which can also account for the ultimate formation of mullite.

The situation in PC/B is somewhat different. The expected products are  $a_2B$ ,  $a_3B$ ,

$a_2a_3B$ ,  $b_1a_2$ , and  $b_1a_3$ . The reactions involving  $a_3$  are as before kinetically impeded and therefore no silicate is formed. Upon heating,  $b_1a_2$  leads once again to the spinel, as in the base-catalyzed reactions. Since the base catalyst conditions the gel structure in such a way that an initial segregation containing  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  is also not formed, mullite is not formed at all. Spinel, being the only product containing  $\text{Al}_2\text{O}_3$ , reacts with  $\text{SiO}_2$  at high temperatures to produce  $\alpha$ -cordierite. We thus see the persistence of traces of spinel even at  $1400^\circ\text{C}$ , much the same way as persistence of mullite in acid-catalyzed PC/A at high temperature.

#### Structure of CZ 20/A

We may now consider the nature of reactions in CZ 20/A, which is very similar to the PC/A except for the added  $\text{ZrO}_2$ . The

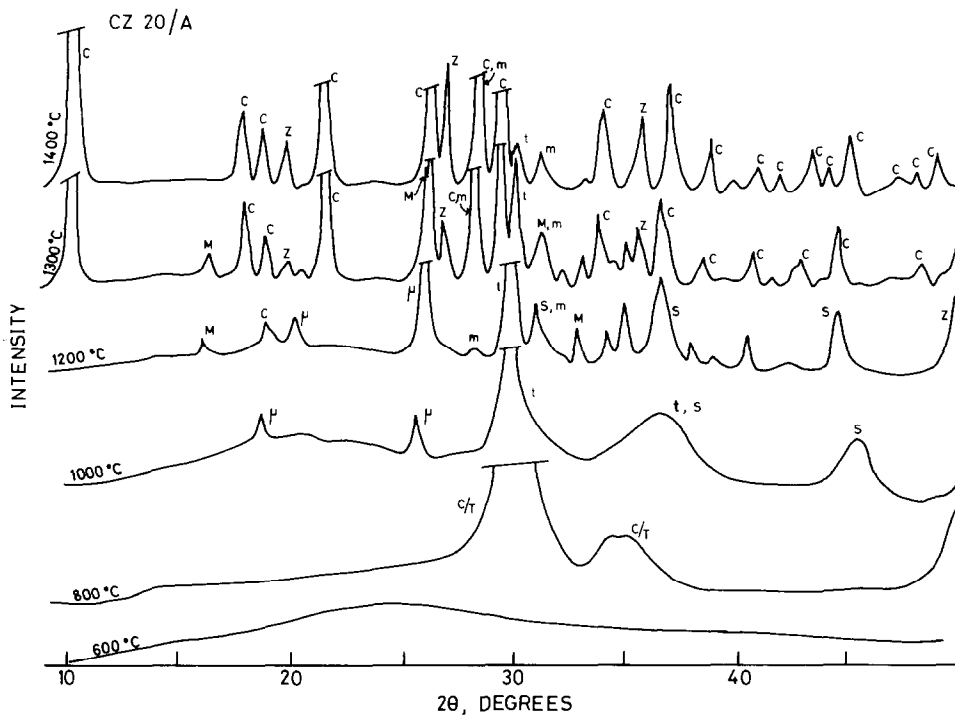


FIG. 4. XRD pattern of CZ 20/A gel heat treated at different temperatures (C,  $\alpha$ -cordierite; t, tetragonal  $ZrO_2$ ; m, monoclinic  $ZrO_2$ ; M, mullite; S, spinel;  $\mu$ ,  $\mu$ -cordierite)

X-ray diffraction patterns obtained after various heat treatments are shown in Fig. 4. We note, in order to discuss the reactions of CZ 20/A, that  $ZrO_2$  itself is nearly as basic as  $Al_2O_3$ ; they tend to form solid solutions at very high temperatures (15). Further, MgO readily reacts with  $ZrO_2$  although up to fairly high concentrations it only forms a solid solution (16), in the latter forming t- $ZrO_2$ . This particular step is a key feature of the sol-gel route for the preparation of cordierite- $ZrO_2$  composites. Reaction of MgO with  $ZrO_2$  occurs at the gel stage itself stabilizing the tetragonal form of  $ZrO_2$  and this will not occur as readily in other preparative techniques (6). Hence we expect the reaction products for CZ 20/A up to 1200°C to be similar to those in PC/A except for the presence of t- $ZrO_2$ , which is borne out very clearly in Table I. At this temperature we

should expect reactions between spinel and  $\mu$ -cordierite to produce  $\alpha$ -cordierite and also small amounts of mullite. We do not expect mullite to be retained permanently as a separate phase, because it will continue to react with spinel to produce  $\alpha$ -cordierite, which is thermodynamically the most stable phase. Since the temperatures are sufficiently high, reaction between  $SiO_2$  and  $ZrO_2$ , which produces zircon, also occurs. Formation of zircon cuts into the availability of  $SiO_2$  for quantitative formation of  $\alpha$ -cordierite and gives the suspicion that this may be the reason for the formation of mullite at high temperatures. However, we recognize that mullite appears at lower temperatures as an independent phase and zircon forms only at higher temperatures. Also, formation of zircon is often assisted (11) by the mullite. Hence mullite is likely to be an

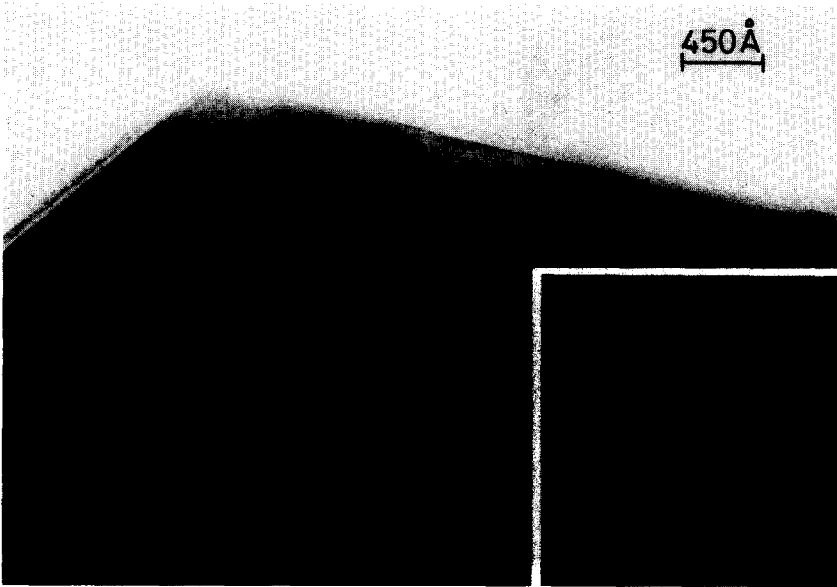


FIG. 5. TEM micrograph of PC/A heat treated at 1400°C confirming the major phase as  $\alpha$ -cordierite. Inset shows  $\langle 142 \rangle$  zone axis diffraction pattern of  $\alpha$ -cordierite.

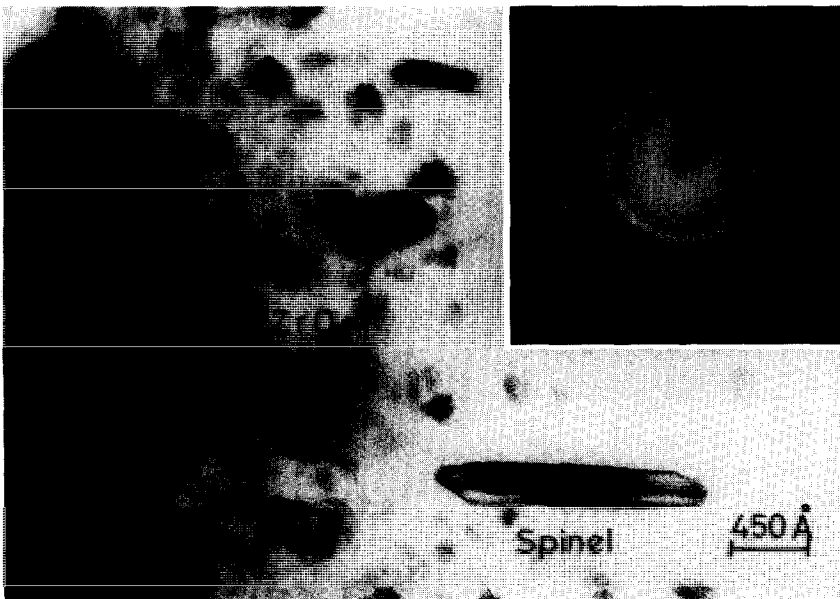


FIG. 6. TEM micrograph of CZ 20/A heat treated at 1200°C showing the presence of needle-shaped spinel and circular  $c/t$ -ZrO<sub>2</sub> particles. Inset shows the polycrystalline diffraction pattern of  $t$ -ZrO<sub>2</sub>.

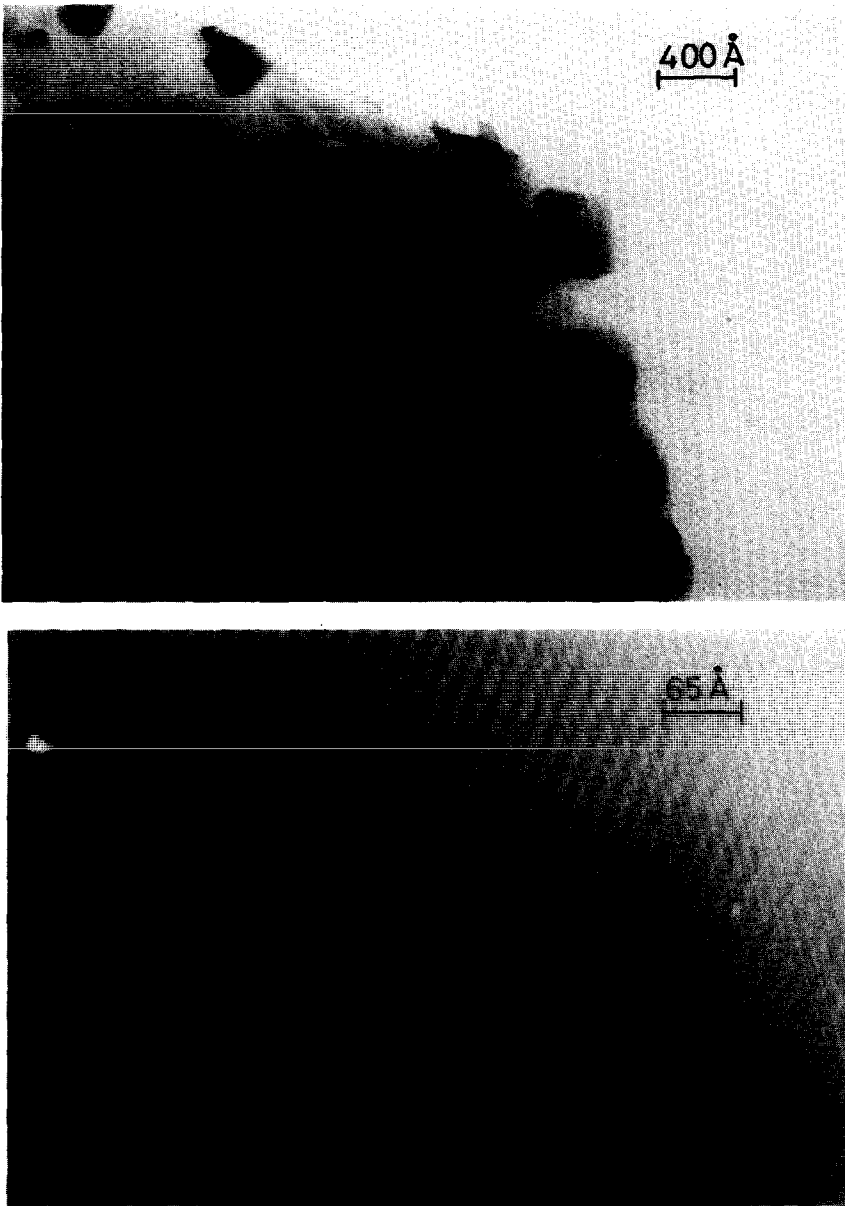


FIG. 7. TEM micrograph of (a) fine-faceted t-ZrO<sub>2</sub> particles, (b) the matrix phase adjacent to a single ZrO<sub>2</sub> particle showing lattice fringes corresponding to  $\alpha$ -cordierite in CZ 20/A gel heat treated at 1300°C (see text).



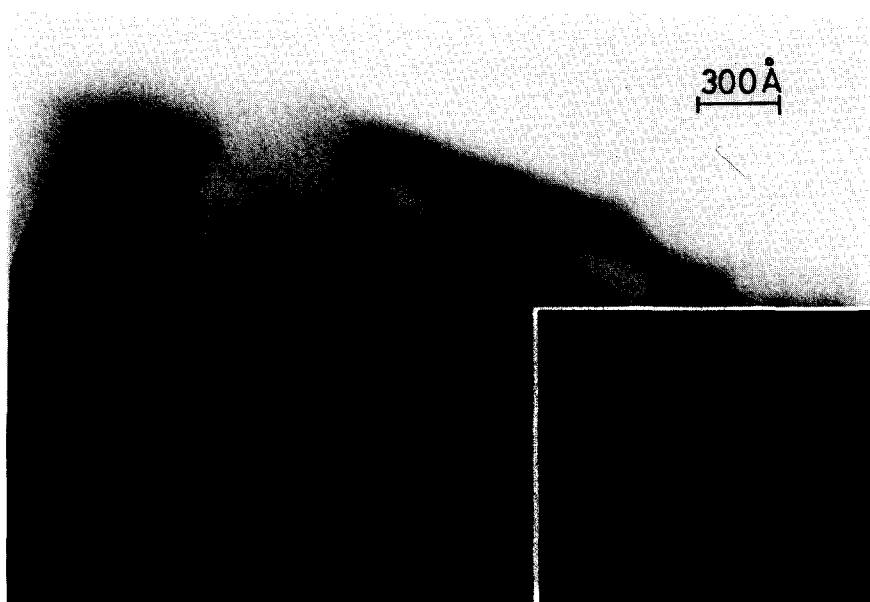


FIG. 8. TEM micrograph of CZ 20/A gel heat treated at 1300°C showing a wavy intergrown phases corresponding to  $\alpha$ -cordierite and cordierite-mullite solid solution. The dark and (faceted) white particles may correspond to  $\text{ZrO}_2$  and zircon. Inset shows the composite diffraction pattern; the bigger spots correspond to the  $\langle 210 \rangle$  zone axis of mullite and the smaller spots correspond to the  $\langle 020 \rangle$  zone axis of  $\alpha$ -cordierite.

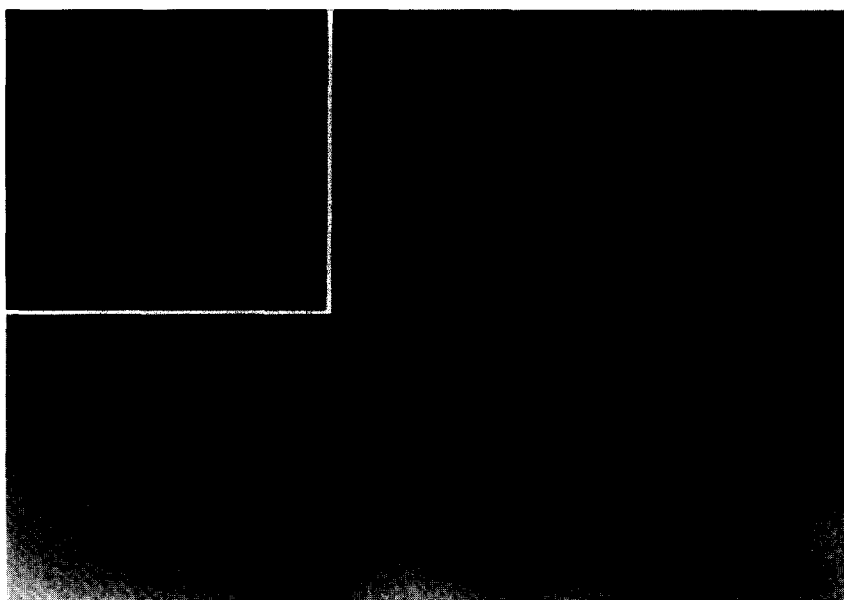


FIG. 9. High resolution lattice of  $\alpha$ -corderite along the  $\langle 010 \rangle$  zone axis in CZ 20/A gel heat treated at 1300°C. Inset shows the corresponding diffraction pattern. The interfringe distance corresponds to 4.2 Å.

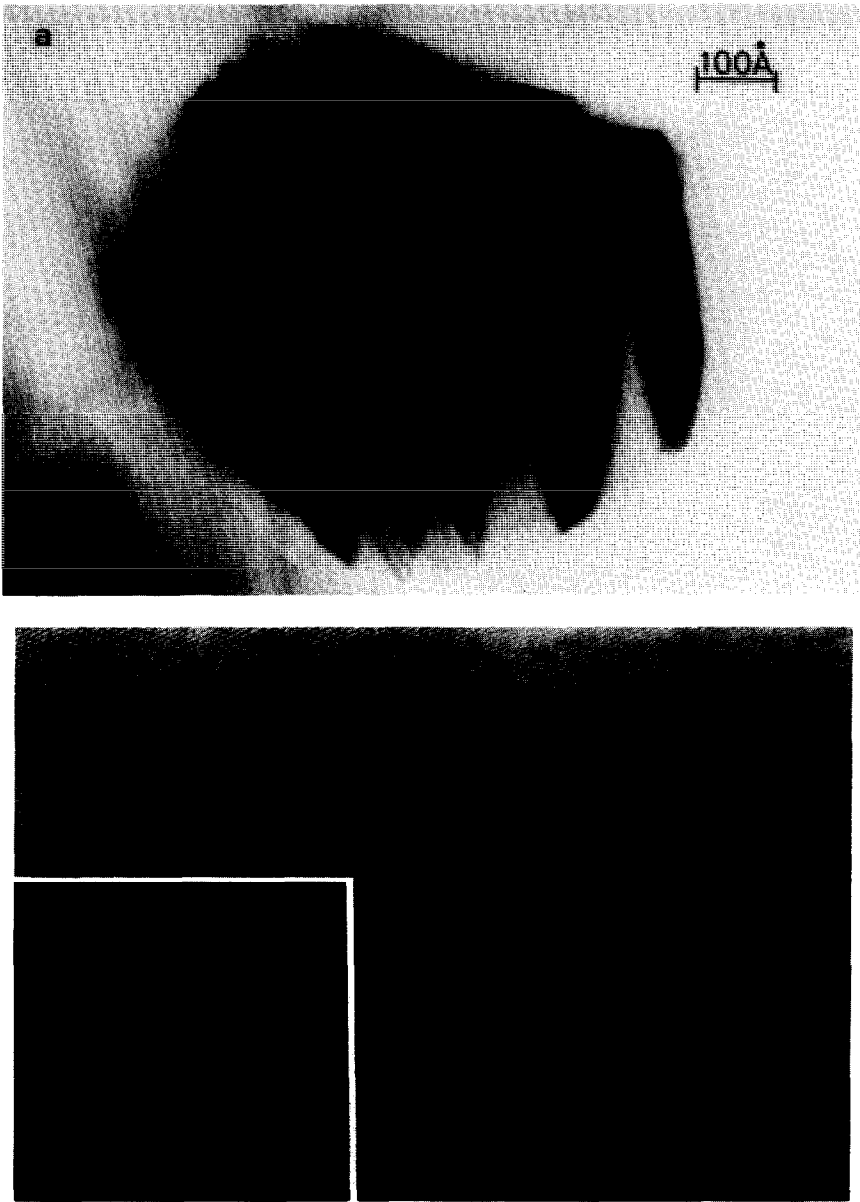


FIG. 10. TEM micrograph of CZ 20/A gel heat treated at 1400°C showing (a) a single-twinned  $m\text{-ZrO}_2$  particle (b) lattice image of a zircon particle resolved in both axis. Inset (b) shows the corresponding diffraction pattern of zircon taken along  $\langle 1\ 2\ 0 \rangle$  zone axis.

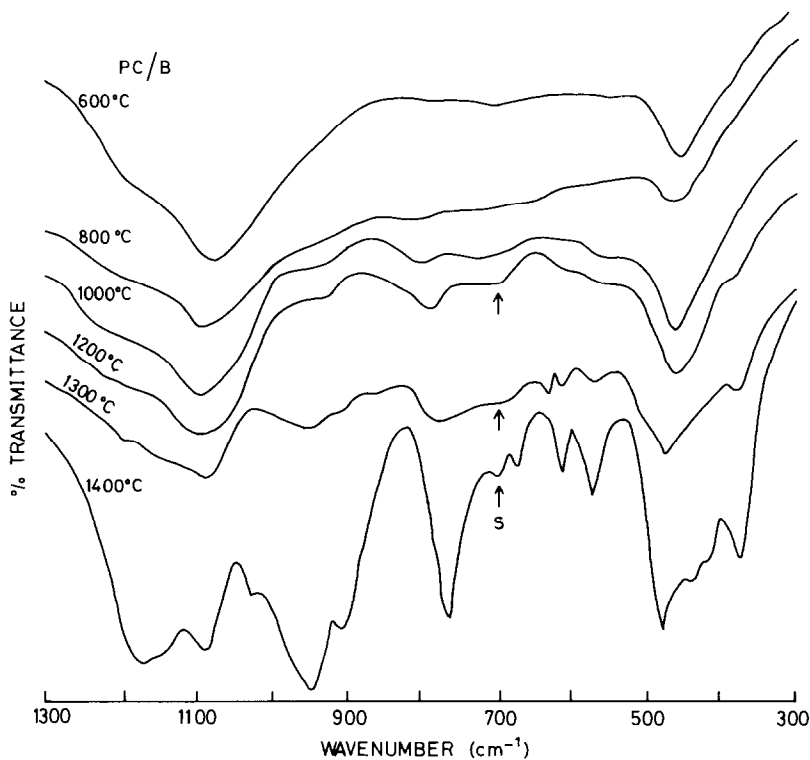


FIG. 11. IR spectra of PC/B gel heat treated at different temperatures (the arrow shows the presence of spinel (S) phase).

intermediate phase which only assists the formation of zircon but at still higher temperature it reacts with spinal to form  $\alpha$ -cordierite (at 1300°C). The presence of traces of m-ZrO<sub>2</sub> at 1300–1400°C suggests that during reaction between spinel and  $\mu$ -cordierite, some 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. Another aspect which deserves attention is the possible formation of solid solution of mullite in cordierite, since there have been references to this in the literature (17), although  $\alpha$ -cordierite and mullite possess different crystal structures. 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. The disappearance of mullite at 1400°C and leaching of MgO from some of the ZrO<sub>2</sub> grains, which therefore transform into monoclinic phase during cooling, supports such a possibility.

#### Evolution of Microstructures

The microstructure of PC/A heated at 1400°C is shown in Fig. 5. The diffraction pattern (zone axis, Z.A.  $\langle \bar{1}42 \rangle$ ) suggests that the major product is  $\alpha$ -cordierite. Although X-ray diffraction indicated the presence of traces of mullite and spinel at 1400°C, it was difficult to identify their presence through electron microscopy. The microstructures of CZ 20/A composite at various temperatures are presented in Figs. 6–10. At 1200°C, Fig. 6 reveals the presence of needles of spinels  $\sim 0.2 \mu\text{m}$  in size. The small circular

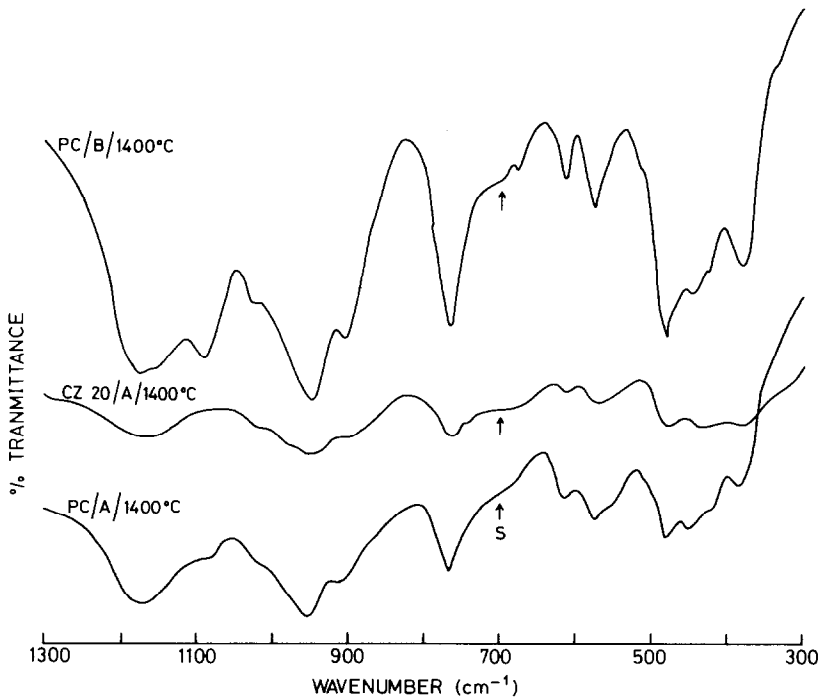


FIG. 12. IR spectra of PC/A, PC/B, and CZ 20/A gels heat treated at 1400°C (the arrow indicates the presence of spinel (S) phase).

dark spots in Fig. 6 are attributed to  $t\text{-ZrO}_2$  present at this temperature. At 1300°C the micrograph shown in Fig. 7a very clearly reveals the formation of faceted particles of  $t\text{-ZrO}_2$ . The lattice image of the surrounding region is shown in Fig. 7b. In the fringe pattern the interfringe distance is  $\sim 18.4 \text{ \AA}$ , which is very close to twice the interplanar spacing in  $\alpha\text{-cordierite}$  ( $C = 9.3 \text{ \AA}$ ) along the  $c$ -axis. The micrograph of yet another region of the same sample in Fig. 8 shows a wavy spread of at least two different phases into each other. The dark and (faceted) white particles inside this biphasic region could be  $\text{ZrO}_2$  and zircon. The wavy intergrown phases correspond to cordierite and the cordierite–mullite solid solution referred to earlier. The corresponding diffraction pattern shows that the bright spots correspond to mullite (Z.A. of the pattern is

$\langle 210 \rangle$ ). The smaller spots in the diffraction pattern were organized into many possible patterns and analyzed for the causative interplanar distances in both mullite and cordierite. One of the possibilities is that they arise from an  $\alpha\text{-cordierite}$  phase with the Z.A. of diffraction being  $\langle 020 \rangle$ . However, it was not possible to account for all the spots present in the diffraction pattern. A thin section of composite was examined using HREM and the image is shown in Fig. 9. From the diffraction pattern we identify the phase as  $\alpha\text{-cordierite}$  (Z.A.  $\langle 010 \rangle$ ). The interplanar distance calculated from the lattice image is  $4.2 \text{ \AA}$  and is in good agreement with the crystal structure (18) data. Zircon and monoclinic  $\text{ZrO}_2$  could be identified in CZ 20/A heated to 1400°C. A region of monoclinic  $\text{ZrO}_2$  consisting of typical twinning bands arising from the shear structure trans-

formation during cooling is shown in Fig. 10a. The formation of monoclinic  $ZrO_2$  has been described earlier. Particles of zircon were identified in a neighboring region. The selected area diffraction pattern and a high resolution image of this region are shown in Fig. 10b. The image is a two-axis reconstruction and interplanar distances have been found to be 4.5 Å. In the inset the diffraction pattern for the same is given, where the bright spots correspond to  $(1\bar{2}0)$  Z.A of zircon. The minor spots which are present exactly between the bright spots arise from the other orientation. Hence the electron microscopy of the composites confirms the presence of all the major phases in the composites indicated in X-ray diffraction studies.

#### *Infrared Spectroscopy (IR)*

IR spectra of cordierite containing mullite have been reported in the literature (17). We have compared in this work the temperature evolution of IR spectra of the gels in the background of literature reports. Figure 11 is typical of the evolution of IR spectra when a PC/B gel is heated to 1400°C. The characteristic  $\alpha$ -cordierite peak is the one at 780  $cm^{-1}$  and the peaks at 530 and 700  $cm^{-1}$  correspond uniquely to spinel. Other peaks are convolutes of the spectra of several phases and do not yield unequivocal information. The cordierite spectrum obtained from PC/B at 1400°C has sharp features and the 780- $cm^{-1}$  peak is quite intense. IR spectra of PC/A and CZ 20/A heated to 1400°C are compared with that of PC/B in Fig. 12. In PC/A and also in CZ 20/A the 780- $cm^{-1}$  peak is significantly lower in intensity than in PC/B. This may be considered as additional evidence for formation of solid solution of mullite in cordierite. Similarly the presence of traces of spinel in PC/A and PC/B (a broad shoulder) may be compared with its virtual absence in CZ 20/A. Nevertheless it is difficult to compare IR spectra of CZ 20/A with those PC/A and PC/B since

the presence of monoclinic and tetragonal  $ZrO_2$  in CZ 20/A broadens most of the important peaks in the CZ 20/A spectra (Fig. 12).

#### **Conclusions**

Cordierite has been prepared by the gel route and examined both in its pure form and in a composite with 20 wt%  $ZrO_2$ . Pure cordierite was prepared by both acid- and base-catalysed sol-gel reactions, whereas the composite was prepared by an acid-catalyzed reaction. We have confirmed that acid/base catalysis conditions the nature of reactions and products: mullite is not formed in base-catalyzed reactions. Spinel occurs as an intermediate phase which ultimately reacts with  $\mu$ -cordierite at high temperatures to produce  $\alpha$ -cordierite;  $\alpha$ -cordierite itself is formed at temperatures >1200°C only. Zircon is formed in the composites and  $ZrO_2$  is mostly present as particulates with (c/t) structure. There is evidence for the possible solid solution formation of cordierite and mullite. Further,  $ZrO_2$ , which is stabilized at the gel stage in the tetragonal phase by reacting with MgO, partly reconverts to pure  $ZrO_2$  at higher temperatures by exsolution of MgO, which is evidenced by the presence of grains of monoclinic  $ZrO_2$  with  $\alpha$ -cordierite in CZ 20/A samples heated to 1400°C.

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