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Aqueous sol–gel synthesis of cordierite and cordierite–zirconia composite powders

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Pure cordierite and cordierite–zirconia (5 and 15 mol.%) are prepared by an aqueous sol–gel technique starting from aqueous solutions of magnesium formate, aluminium formate, zirconium formate and tetraethoxysilane. The gels are dried and calcined at different temperatures ranging from 600 to 1300 °C. The dried gels and calcined powders are characterized by thermogravimetric analysis, differential thermal analysis, X-ray powder diffraction and infrared spectroscopic analysis.

1. Introduction

Cordierite and cordierite-based glass ceramics are used as structural materials for their properties of low thermal expansion, good thermal shock resistance, low density and low thermal conductivity. They are also used as electronic packaging substrates due to their low dielectric constants [1–4]. Conventionally, cordierite ceramics are prepared by calcination of a mixture of clays, talc and aluminium hydroxide, or by devitrification of a cordierite glass of suitable composition. However, sintering is also difficult without any sintering aid [3] because of the narrow sintering temperature range. The mechanical properties of the products are therefore relatively poor. Recently, pure and crystalline cordierite powders have been prepared by a sol–gel method. For the synthesis of the multicomponent silicate powders from metal alkoxides, chemical homogeneity of the powder has great importance. Different hydrolysis rates of individual alkoxides may result in chemical inhomogeneity in the hydrolysis products leading to higher crystallization temperature or undesired crystalline phases [5]. To overcome this limitation, several approaches have been attempted, including matching of hydrolysis rates by chemical modifications with chelating ligands [6–8] and synthesis of multication alkoxides [9] or partial prehydrolysis of an alkoxide [10, 11]. In the cordierite system, Hardey *et al.* [5] and McMahon [9] carried out the synthesis of a multication complex alkoxide containing three elements in the stoichiometric ratio. As all the above approaches are very complex in nature, we have initiated a simple approach of aqueous sol–gel technique, for the synthesis of cordierite and cordierite–zirconia composites.

In all the sol–gel syntheses reported above, alcohol was used as the common solvent for the precursors of the gel. Since the preparation of silica [12, 13], ZrO_2–SiO_2 [14] and mullite [15] gels in aqueous medium have been reported, we have now successfully used water as an efficient solvent for metal formates and tetraethoxysilane (TEOS) which are used as precursors in the synthesis of cordierite and cordierite–zirconia composites.

2. Experimental procedure

Details of the raw materials are given below:

Tetraethoxysilane (98 wt%), Fluka Chemika

Zirconium oxychloride octahydrate (98 wt%), Aldrich Chemicals

Aluminium nitrate nonahydrate (98.5 wt%), BDH Chemicals, India

Magnesium nitrate hexahydrate (98.5 wt%)

Formic acid (85 wt%), Qualigen Fine Chemicals, India.

Freshly precipitated aluminium hydroxide, magnesium hydroxide and zirconium hydroxide are prepared by adding ammonium hydroxide to the corresponding metal salt solution. These hydroxides are then reacted with aqueous formic acid solution to give the corresponding metal formate solutions. Metal formate solutions containing the required amount of metals are then added to TEOS according to the composition. The specific conditions and experimental details are listed in Table I. At the beginning of mixing, TEOS and the aqueous solutions of metal formates are immiscible. A homogeneous solution is obtained after about 20 min of hydrolysis of TEOS under rapid stirring. Slow stirring and heating is continued until the formation of a gel.

The gels are dried at 100 °C for 24 h on a waterbath and then ground to powders. These powders are gradually heated at 5 °C min^{-1} and are calcined in air for 1 h to 12 h to temperatures ranging from 600 to 1300 °C. Infrared spectra of these samples are obtained in KBr medium using Perkin–Elmer 883 spectrophotometer. Room temperature X-ray diffraction (XRD) patterns are obtained using a Philips X-ray

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TABLE I Experimental details of the preparation of gels of the cordierite and cordierite–zirconia systems

Composition	Sample[a]	Vol.[b] (ml)	pH[c]	Time[d] (h)
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$	CZO	60	1.1	2
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ with 5 wt% ZrO_2	CZ5	80	1.2	3
$2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$ with 15 wt% ZrO_2	CZ15	100	1.4	5

[a] In all the sample solutions, the amount of TEOS used is 10 ml (0.04389 mole) and the amount of other constituents are according to their molecular proportions. Aqueous formic acid is used to make the metal formate solution.

[b] Initial volume of the sample solution including TEOS.

[c] Initial pH of the sample solution after adding TEOS to the mixed metal formate solution.

[d] Average time required for the formation of gel for each sample prepared three times. Temperature is maintained at 60 °C throughout the formation of gel.

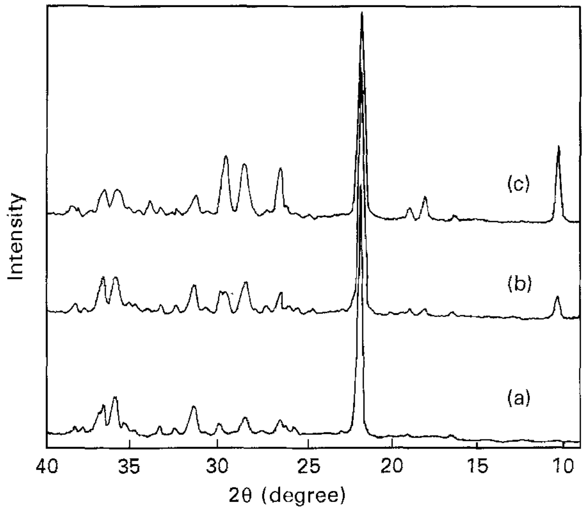

Figure 1 Room temperature powder XRD patterns of the sample CZO after calcination at 1200°C for (a) 1 h, (b) 6 h, (c) 12 h.

powder diffractometer PW 11710 and Cu$K\alpha$ radiation. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) runs are taken at a heating rate of 10 °C min^{-1} in air using a Shimadzu DT-40 thermal analyser.

3. Results

TGA of dried gel powders exhibits three step weight losses. The total weight loss in the dried gel amounts to about 40 wt%. There is no significant weight change beyond 550 °C. The DTA curves show a small endothermic peak at about 60 °C, a large endothermic peak at about 150 °C and an exothermic peak at 390 °C.

Room temperature XRD patterns for all the three samples calcined at different temperatures were taken and some selected patterns are shown in Figs 1–4. All the dried gel powders are amorphous to XRD and the amorphous nature is retained when the gel powders are calcined up to 600 °C. The crystalline phases of all

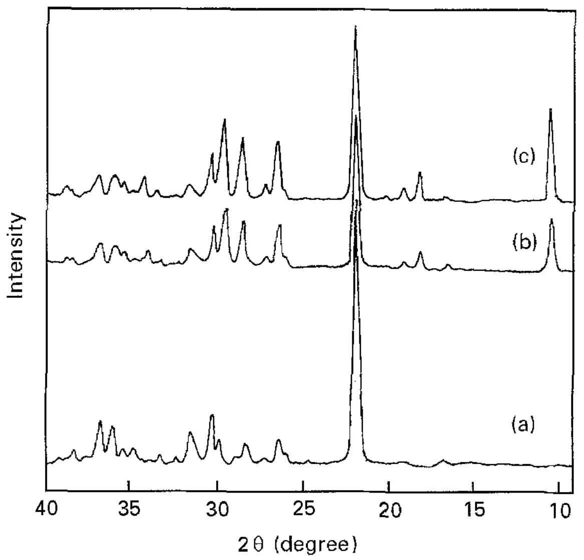

Figure 2 Room temperature powder XRD patterns of the sample CZ5 after calcination at 1200°C for (a) 1 h, (b) 6 h, (c) 12 h.

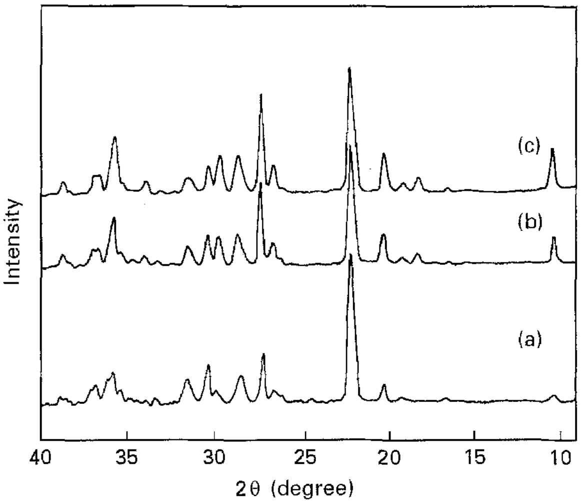

Figure 3 Room temperature powder XRD patterns of the sample CZ15 after calcination at 1200°C for (a) 1 h, (b) 6 h, (c) 12 h.

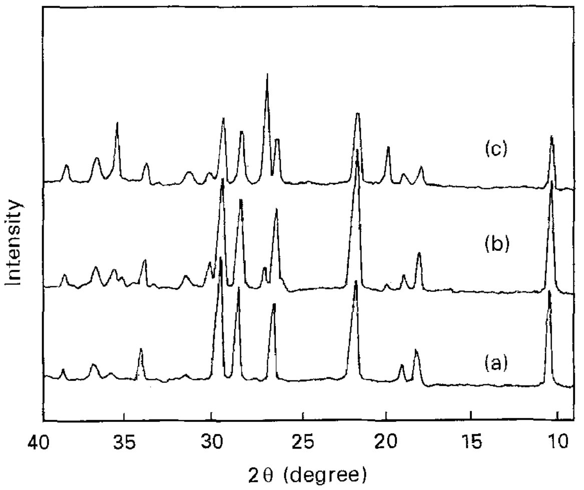

Figure 4 Room temperature powder XRD patterns of the samples after calcination at 1300°C for the (a) CZO, (b) CZ5, (c) CZ15.

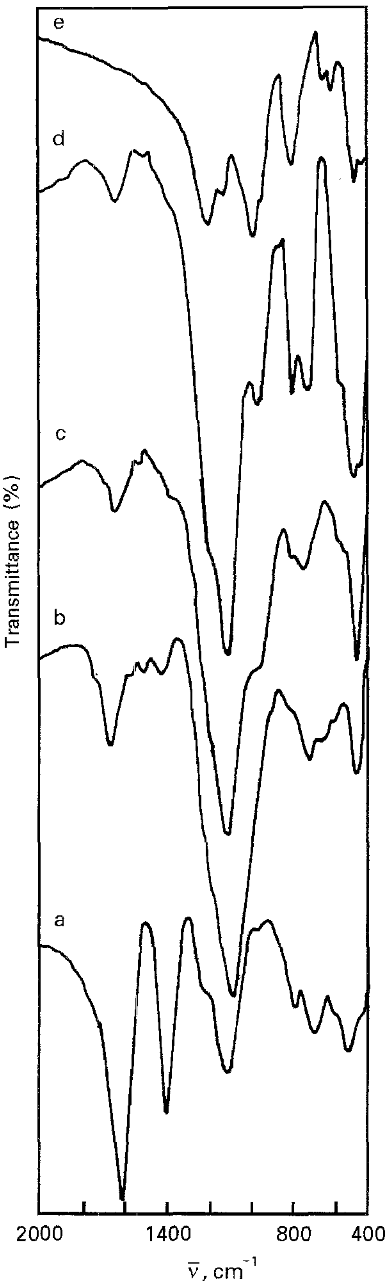

Figure 5 IR spectra of the sample CZ5 (a) dried powder at 100°C and after calcination for 1 h at (b) 600°C, (c) 900°C, (d) 1100°C, (e) 1300°C.

the samples calcined at different temperatures for 1 h are summarized in Table II. Sample CZO produces spinel and μ-cordierite and samples CZ5 and CZ15 produce spinel, μ-cordierite and tetragonal zirconia as initial phases of crystallization when calcined at 900 °C for 1 h. When samples are calcined at 1200 °C, μ-cordierite starts to convert into α-cordierite. Small amounts of spinel and cristobalite are still present. The complete formation of α-cordierite with the disappearance of spinel and cristobalite is observed for sample CZ0 calcined at 1300 °C. Samples CZ5 calcined at 1300 °C show the characteristic peaks of zircon and tetragonal zirconia together with α-cordierite.

Figs 5–7 show the infrared (i.r.) spectra of samples CZ0, CZ5 and CZ15 after calcination at different temperatures. In the gel powders dried at 100 °C, principal absorption bands of formate and hydroxyl groups are observed without any significant presence of absorption bands due to amorphous silica. I.r. spectra of the samples calcined at 1200 °C and 1300 °C show the characteristic bands of cordierite, zircon and zirconia.

TABLE II Summary of X-ray powder diffraction studies in pure cordierite and cordierite–zirconia composites during heat treatment

	Temperature of heat treatment (1 h) (°C)				
Sample	600	900	1100	1200	1300
CZ0	A	μ S	μ S X	μ + C S X	C
CZ5	A	μ S t	μ S t X	μ + C S t X	C Z t
CZ15	A	μ S t	μ S t x m	μ + C S t x	C Z t

A, amorphous; S, spinel; μ, μ-cordierite; X, cristobalite, t, tetragonal zirconia; m, monoclinic zirconia; Z, zircon; C, α-cordierite.

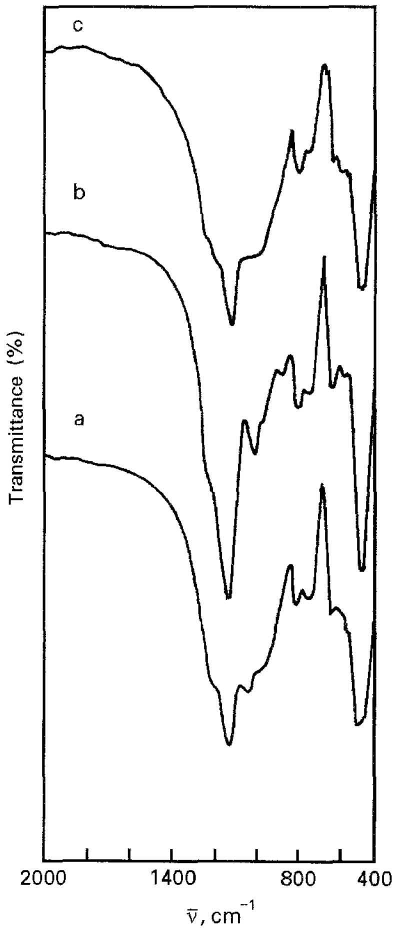

Figure 6 IR spectra of the sample after calcination at 1200°C for 1 h (a) CZO, (b) CZ5, (c) CZ15.

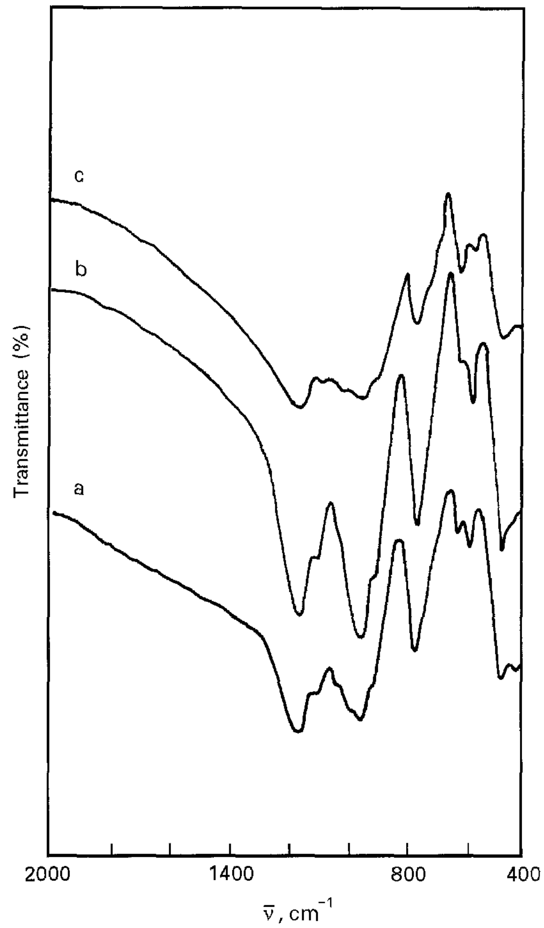

Figure 7 IR spectra of the sample after calcination at 1300°C for 1 h (a) CZ0, (b) CZ5, (c) CZ15.

4. Discussion

The stable phase of cordierite is known to be α-cordierite and is present in most cordierite ceramics. It has a hexagonal crystal structure. The other phases in the MgO–Al_2O_3–SiO_2 system which are associated with this are mullite ($3Al_2O_3 \cdot 2SiO_2$), spinel ($MgO \cdot Al_2O_3$) and forsterite ($2MgO \cdot SiO_2$). In the MgO–Al_2O_3–SiO_2–ZrO_2 system in which ZrO_2 is also present, the other phase formed is zircon ($ZrO_2 \cdot SiO_2$). A small amount of zirconia is also present in the calcined composite powders.

From these results, a possible reaction sequence could be as follows. In sample CZO, initially formed μ-cordierite, spinel and cristobalite react to produce α-cordierite at 1300 °C. A small amount of mullite, formed initially, also reacts with spinel to produce α-cordierite. In order to discuss the reactions in CZ5 and CZ15 samples, we note that ZrO_2 itself is nearly as basic as Al_2O_3. The two tend to form solid solutions at high temperature [16]. Further MgO readily reacts with ZrO_2 to form a solid solution [17] along with the formation of t-ZrO_2. This is a very important feature of the sol–gel preparation of cordierite–zirconia composites. Formation of stabilized zirconia is possible due to atomic level mixing of the constituent elements in the solution and therefore also in the gel, which is not possible for the normal solid-state method [18] at low temperatures. It is clear from Table II that the reaction products for CZ5 and CZ15 samples are almost similar to those of the CZO system except for the presence of zircon and t-ZrO_2. The temperature of 1300 °C is sufficiently high for the reaction between ZrO_2 and SiO_2 to occur, leading to the formation of zircon.

The characteristic i.r. spectroscopic band for -cordierite at 780 cm^{-1} [19] is present in all the samples calcined at 1300 °C. The i.r. spectroscopic bands at 530 and 700 cm^{-1} which correspond to spinel are absent in all the samples calcined at 1300 °C. The i.r. spectra of the CZ5 and CZ15 samples calcined at 1300 °C show the characteristic peak of zircon at 610 cm^{-1} which is consistent with the observations of the XRD studies.

5. Conclusions

Cordierite and the cordierite–zirconia composites are easily obtained by aqueous sol–gel synthesis. The formation of cordierite at comparatively low temperatures is due to atomic scale mixing of the constituent elements in solution and in the gel. This method is cheaper, technically simpler and more time-efficient than other reported sol–gel methods for the preparation of these materials.

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