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Aqueous sol–gel synthesis of mullite powder by using aluminium oxalate and tetraethoxysilane

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Gels with the composition of mullite ($3Al_2O_3$–$2SiO_2$) were prepared from an aqueous solution of aluminium oxalate and tetraethoxysilane. High-purity stoichiometric mullite powders were produced by calcination of the gel powders with a small exothermic event at 1250 °C. The chemical and structural evolutions were characterized as a function of heat treatment by differential thermal analysis (DTA), thermogravimetric analysis (TGA), X-ray powder diffraction (XRD) and infrared (i.r.) spectroscopy. The composition of mullite varied with the temperature of the heat treatment.

1. Introduction

Mullite ($3Al_2O_3$–$2SiO_2$) is a promising refractory [1] for high-temperature structural ceramics application because of its low thermal expansion [2] and high creep resistance [3]. It is a characteristic constituent of traditional ceramics made from aluminosilicate and is well-known as the only stable compound in the Al_2O_3–SiO_2 system, which melts incongruently at 1828 °C [1]. It is usually made by the reaction of mixed alumina and silica powders or mineral precursors at 1600–1700 °C for several hours. The products commonly have a variable composition so that sintered bodies contain an excess of alumina or silica as a second phase [4].

According to recent studies [5], mullite ceramics show little degradation in their flexural strength (above 350 MPa) up to 1300 °C because of their highly covalent character. Sintered mullite is also attractive for its potential application in infrared (i.r.) windows [6] or low-expansion-substrate manufacturing [7]. However, mullite is difficult to sinter into full density and high-purity stoichiometric bodies. To overcome these limitations, attempts have been made to prepare mullite with a more uniform composition and at lower temperature from powders via chemical routes such as coprecipitation, sol–gel or spray-pyrolysis methods [8–20].

In all the reported sol–gel syntheses of mullite, alcohol have been used as the common solvent for the precursors of the gel. Our aim was to simplify the sol–gel method for the synthesis of gels in the mullite system. Since the preparation of silica [21, 22] and ZrO_2–SiO_2 [23] gels in aqueous media have been reported, we have applied water successfully as an efficient solvent for aluminium oxalate and tetraethoxysilane (TEOS).

2. Experimental procedure

2.1. Raw materials

The details of the raw materials are: (a) TEOS (assay > 98 wt %) Fluka Chemika; (b) aluminium nitrate, nonahydrate (> 98 wt %) Aldrich Chemicals; and (c) oxalic acid (> 99.5 wt %), E. Merk (India) Ltd.

Aluminium hydroxide was completely precipitated from an aluminium-nitrate nonahydrate solution by adding ammonium hydroxide. The solution was filtered and the precipitate washed with water several times. This precipitated aluminium hydroxide was dissolved in an aqueous oxalic-acid solution using excess oxalic acid (1:2 molar ratio) by warming it in a waterbath (at 100 °C) to obtain a clear aluminium-oxalate solution. This solution was evaporated to dryness on the waterbath to obtain the solid aluminium-oxalate precursor.

Additionally, part of this aluminium oxalate was ground and calcined in air, at 900, 1100 and 1300 °C for 1 h in each case. These pure-alumina powders and the solid aluminium oxalate were subsequently characterized by powder X-ray diffraction (XRD) and i.r. spectroscopic analysis as references.

2.2. Preparation of the gels and powders

Gels with the composition of mullite, $3Al_2O_3$–$2SiO_2$ were prepared from an aqueous aluminium-oxalate solution and TEOS. The specific conditions and experimental details are listed in Table I. Initially, a mixture of TEOS and aluminium-oxalate solution were immiscible. A homogeneous solution was obtained after about 30 min of hydrolysis of the TEOS under continuous magnetic stirring. The slow stirring and heating was continued until the gel formed.

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TABLE I Preparative conditions for the formation of mullite gels

Sample[a]	Temperature (°C)[b]	t_{gel} (h)[c]
M1	50	46
M2	60	22
M3	70	10

[a] In all the sample solutions, the amount of TEOS was 10 ml (0.04389 mole) and the amount of aluminium oxalate was determined by the molar ratio of mullite. The amount of water used to make the aluminium-oxalate solution was 80 ml in each case.
[b] The temperature during the formation of the gel.
[c] The average gelation temperature for each sample prepared three times.

The gels were dried at 100 °C for 24 h on the waterbath and then ground to powder. These powders were calcined in air for 1 h at 600, 900, 1000, 1100, 1200 and 1300 °C.

Additionally, pure silica gel was prepared by hydrolysis of TEOS and then it was mixed with solid aluminium oxalate corresponding to the molar ratio of mullite and mechanically ground to powder (sample A3S2). The A3S2 sample was calcined in air for 1 h at 600, 900, 1100 and 1300 °C.

2.3. Characterization of materials

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) runs were made at a heating rate of 10 °C min^{-1} in air using a Shimadzu thermal analyser DT-40. The crystalline phases of the gel powders were identified by a powder XRD pattern which was obtained using a Phillips X-ray powder diffractometer PW 1840 using CuK$_\alpha$ radiation. I.r. spectra of the powders were recorded from 400 to 2000 cm^{-1} using a Perkin Elmer 883 i.r. spectrophotometer. The i.r. samples were prepared using a KBr-pellet method.

3. Results

TGA of the dried gel powders exhibited a three-step weight loss. The total weight loss in the dried gel was 72 wt %. There was little further weight change beyond 400 °C. The DTA curve shows two endothermic peaks at 110 and 345 °C and three exothermic peaks at 375, 990 and 1250 °C.

To understand the sequence of the phase development in the gel powders, pure alumina and the sample A3S2 were calcined at different temperatures; a series of XRD patterns are shown in Figs 1 and 2. The crystalline morphology of the gel powders and the sample A3S2 are given in Table II. All the dried gel powders of the mullite system were amorphous and this phase was retained when the gel powders were calcined up to a temperature of 800 °C. Broad XRD peaks of γ-alumina were obtained when the gel powders were calcined at 900 °C and these peaks were retained when the gel powders were calcined up to 1100 °C. The XRD pattern of the gel powders calcined at 1200 °C shows the mullite phase. The XRD peak

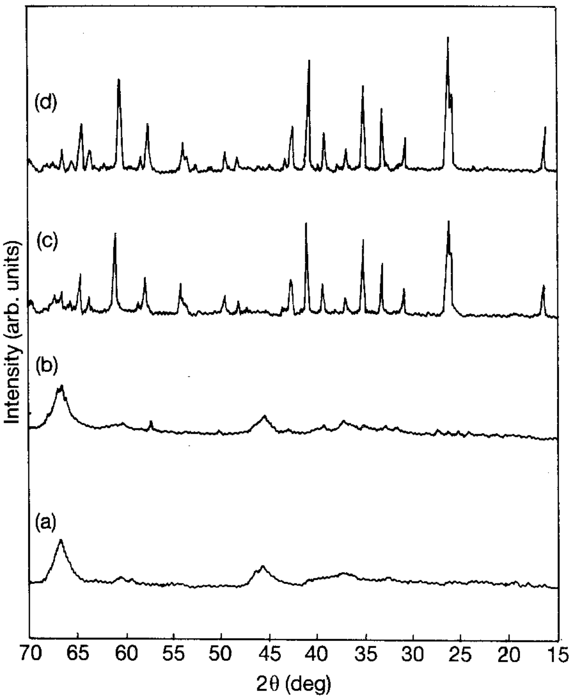

Figure 1. Powder X-ray diffractograms of the sample M1 after calcination for 1 h at temperatures of: (a) 1000 °C, (b) 1100 °C, (c) 1200 °C, and (d) 1300 °C.

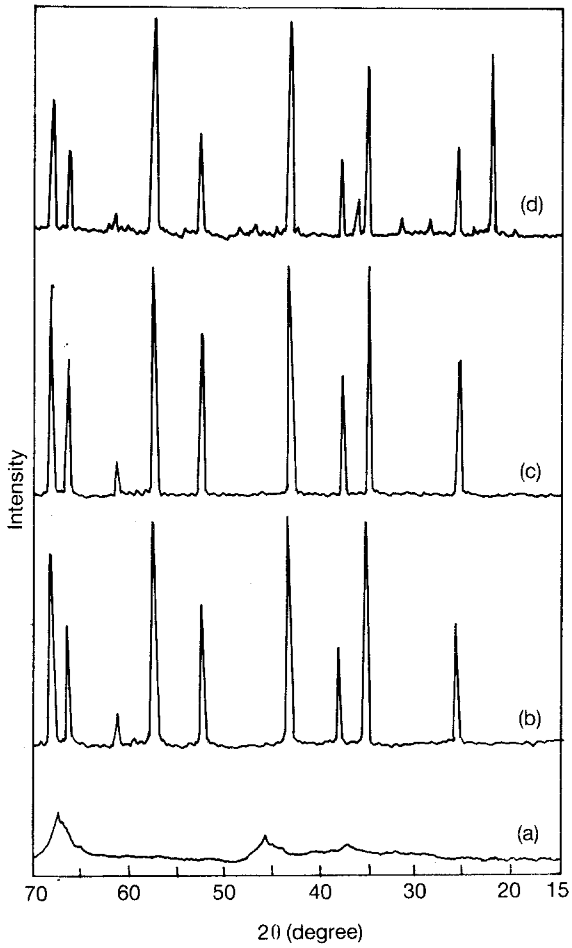

Figure 2. Powder X-ray diffractograms of pure alumina obtained from aluminium oxalate after a calcination for 1 h at temperatures of : (a) 900 °C, (b) 1100 °C, (c) 1300 °C, (d) The sample A3S2 after calcination for 1 h at 1300 °C.

TABLE II The crystal morphology from powder X-ray diffraction analysis of the samples M1 and A3S2 calcined at different temperatures

Sample	Temperature (°C)	Phase[a]
M1	100	A
	900	γ-Al_2O_3
	1100	γ-Al_2O_3
	1200	M
	1300	M
A3S2	100	A
	1300	C + α-Al_2O_3

[a] A, amorphous; M, mullite; and C, cristobalite

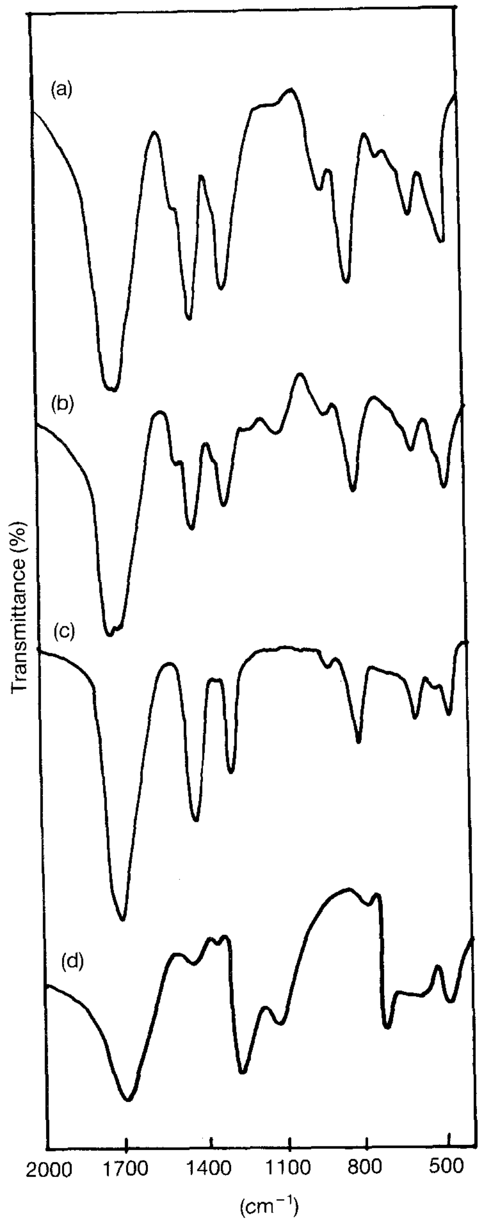

Figure 3. I.r. spectra of the samples: (a) oxalic acid, (b) aluminium oxalate; (c) M1 dried at 100 °C, and (d) A3S2 dried at 100 °C.

intensity was enhanced when the gel powders were calcined at 1300 °C. Pure alumina prepared from aluminium oxalate was amorphous when calcined up to 800 °C. It also showed the γ-alumina phase when calcined upto 1000 °C. Pure alumina calcined at temperatures of 1100 °C and above only showed the α-alumina crystalline phase. The XRD pattern of the sample A3S2 calcined at 1300 °C was a mixture of α-alumina and cristobalite without any significant formation of mullite.

Several of the structural changes in the gel powders calcined at different temperatures were also observed by i.r. spectroscopic analysis. Figs 3 to 5 show the i.r. spectra of the gel precursors, the gel powders and the A3S2 sample heated and calcined at different temperatures in the wave number range 400–2000 cm^{-1}. In the gel powders, dried at 100 °C, principal absorption bands of aluminium oxalate are present without any significant presence of absorption bands due to amorphous silica. The i.r. spectra of the gel powders calcined at 1200 and 1300 °C show only the characteristic bands of mullite. The respective vibrational frequencies of the gel powders and A3S2 samples and their assignments are summarized in Table III.

4. Discussion

The first DTA endotherm at 110 °C can be explained as being due to the removal of loosely bound or physisorbed water, probably from the relatively large proportion of the sample demonstrated to be amorphous. Noting the relative values of the corresponding weight losses, it can be inferred that the endotherm at

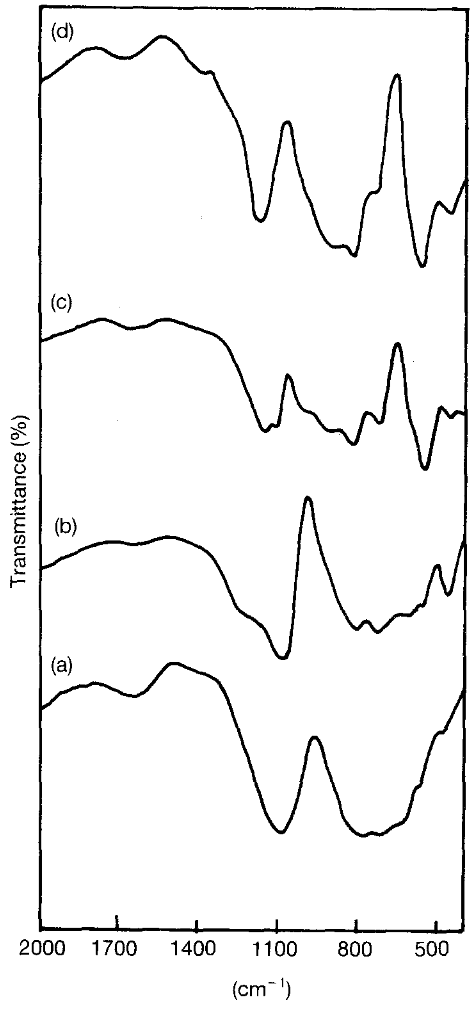

Figure 4. I.r. spectra of the sample M1 after calcination for 1 h at: (a) 900 °C, (b) 1100 °C, (c) 1200 °C, and (d) 1300 °C.

TABLE III I.r. bands (in cm^{-1}) of gel powder (M1) and the sample A3S2

Relevant literature lab. data	Assignment[a]	Temperature (°C)	Sample[b]	
			M1	A3S2
1719 (lab.)	Ox	100	1729 vs	1729 vs
1475 (lab.)	Unknown	100	1475 w	1475 w
1475 (lab.)	Ox	100	1413 s	1415 s
1287 (lab.)	Ox	100	1290 s	1289 s
1175 [29, 30]	Mullite	1200	1171 m, b	
		1300	1173 s	–
1125 [29, 30]	Mullite	1200	1125 w	
		1300	1127 sh	–
1090 [31]	SiOSiTO	100	1100 w	1090 sh
		900	1094 s, b	
		1100	1100 s	
		1300	–	1097 s
932 [29, 30]	Mullite	1200	921 w, b	
		1300	924 w, b	–
916 (lab.)	Ox	100	920 w	917 m
820 (lab.)	Ox	100	821 s	822 s
814 [29, 30]	Mullite	1200	818 m	
		1300	819 m	–
800 [31]	SiOSism	900	800 w, b	
		1100	801 w	
		1300	–	797 m
745 [30]	γ-Al_2O_3	900	750 w, b	
		1100	741 w	
725 [29, 30]	Mullite	1200	728 w	
		1300	721 sh	–
640 [30]	α-Al_2O_3	1300	–	641 sh
600 [30]	α-Al_2O_3	1300	–	601 s
560 [29, 30]	Mullite	1200	559 w	
		1300	562 s	–
485 [29, 30]	Mullite	1200	470 s	
		1300	470 w	–
460 [31]	SiOSibm	900	465 h	
		1100	463 m	
453 [30]	α-Al_2O_3	1300	–	453 s

[a] Ox, aluminium oxalate; SiOSiTO, asymmetric Si–O–Si stretching vibration, transverse optics; SiOSism, network Si–O–Si symmetric stretching vibration; SiOSibm, network Si–O–Si bending vibration.

[b] v, very; w, weak; m, medium; s, strong; sh, shoulder; b, broad.

345 °C is associated with the chemically bound water and the first exotherm at 375 °C is attributed to the decomposition and oxidation of oxalate. The exothermic events occurred in the DTA records at 990 and 1250 °C are characteristic of aluminosilicate minerals [24, 25]. It is generally agreed that for mullite precursors the exothermic event at 990 °C is due to the crystallization of γ-alumina (spinel) [26]. The small exothermic peak at 1250 °C is associated with the formation of mullite as a result of a reaction between γ-alumina and silica.

The morphology of the gel powders remained unchanged with heating up to 800 °C, but crystallization to γ-alumina commenced at about 900 °C and was further developed by 1100 °C. At 1200 °C, fine-grained polycrystalline mullite formed by reaction of γ-alumina with silica after only 1 h of calcination and was further developed at 1300 °C. Rapid formation of mullite within the short time span (1 h) of heating was possible only due to the homogeneous mixing of alumina and silica. On the other hand, after calcination at 1300 °C for 1 h, mullite was not formed at all from the A3S2 sample, but there was a separate phase of α-alumina and crystobalite. This is probably due to the sizes of the crystallites of γ-alumina and the homogeneity of the constituent elements in the two cases: because the reaction can only take place at the surfaces of such crystallites.

Formation of mullite was also supported by i.r. spectroscopic analysis. Cameron [27] and Okada *et al.* [28] reported the chemical composition of mullite as a function of the 1130 and 1170 cm^{-1} absorption bands. When the chemical composition of mullite was rich in alumina, the 1130 cm^{-1} peak was stronger in intensity than the 1170 cm^{-1} peak and the reverse was true as the composition approached 60 mol % alumina. The 1130 cm^{-1} absorption band was comparatively stronger for the gel powder calcined at 1200 °C than for the gel calcined at 1300 °C. The band at 1170 cm^{-1} was much stronger than the 1130 cm^{-1} band for the gel powder calcined at 1300 °C. This sequence of variation in intensity reflects the change in the chemical composition of mullite. With increasing temperature, the composition of mullite progressively approached 60 mol % alumina, the stoichiometric alumina concentration in a mullite composition. The i.r. spectra of the A3S2 sample calcined at 1300 °C showed only the characteristic

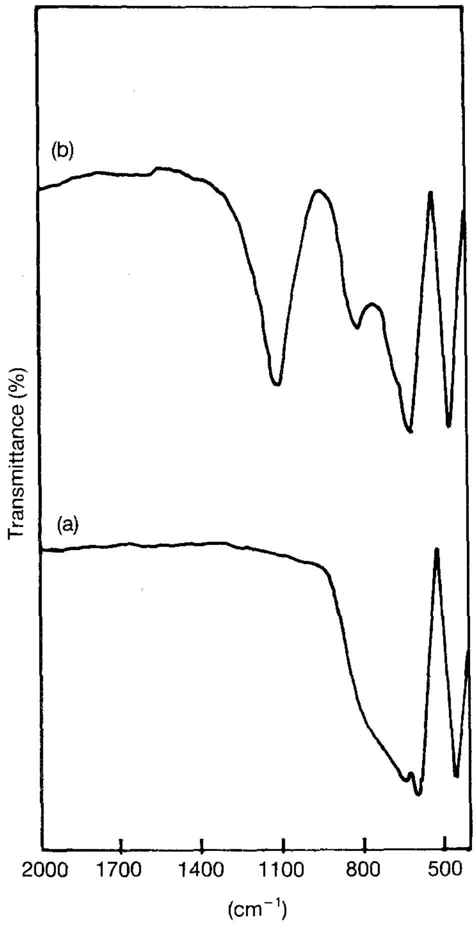

Figure 5. I.r. spectra of the samples after calcination for 1 h at 1300 °C: (a) pure alumina from aluminium oxalate, and (b) A3S2.

absorption bands of silica and α-alumina which supports the results of powder XRD.

5. Conclusion

The combined results of TGA, DTA, XRD and i.r. spectra present a clear formation sequence for obtaining mullite from gel powder starting from an aqueous solution. Formation of mullite occurs after calcination of gel powder at 1200 °C for 1h which is due to the intimate mixing of the constituent elements in the gel powder. This method is comparatively easier, technically simpler, and more time efficient and cost effective than other reported sol–gel methods.

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