



## MICROWAVE-ASSISTED PREPARATION AND SINTERING OF MULLITE AND MULLITE–ZIRCONIA COMPOSITES FROM METAL ORGANICS

**B.G. Ravi, V. Praveen†, M. Panneer Selvam, and K.J. Rao\***

Solid State and Structural Chemistry Unit, Indian Institute of Science,  
Bangalore 560 012, India

(Refereed)

(Received February 9, 1998; Accepted February 19, 1998)

### ABSTRACT

Decomposition characteristics of a mixture of aluminum-tri-sec butoxide (ASB) and tetraethyl orthosilicate (TEOS) in ethyl acetate solution by microwave pyrolysis was examined. The decomposed product was used as a second-stage precursor in the preparation of pure mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ). Mullite–zirconia composites were obtained, using the above mixture along with zirconium-iso-propoxide as starting materials. Pellets of mullite and mullite–zirconia composites were sintered in a microwave oven using  $\beta$ -SiC as a secondary heater. © 1998 Elsevier Science Ltd

**KEYWORDS:** A. ceramics, A. composites, C. thermogravimetric analysis (TGA), C. X-ray diffraction, D. microstructure

### INTRODUCTION

There has been considerable interest in mullite and mullite-matrix composites in recent years due to their unique properties, such as low thermal expansion, low dielectric constant, high melting point, remarkable chemical resistance, high hardness, and excellent creep resistance [1]. These properties have been optimized using a variety of methods for mullite synthesis, for example, sol-gel [2], coprecipitation [3], hydrolysis [4], spray pyrolysis [5], chemical vapor deposition [6], and thermal decomposition [7].

---

\*To whom correspondence should be addressed.

†Undergraduate Research Scholar under exchange program.

Use of microwaves in the synthesis and processing of ceramics has attracted much attention recently because it offers a novel synthetic pathway notable for features such as rapid heating rates, short processing durations, low power requirements, and product uniformity [8–14]. Synthesis of  $\beta$ -SiC [15], AlN [16], MoO<sub>2</sub> [17], and several other materials [13] by the microwave route has already been reported by this laboratory. We also have reported achieving very rapid sintering of ZrO<sub>2</sub>-CeO<sub>2</sub> ceramics using microwave irradiation [18]. Recently, aluminum-tri-sec butoxide and zirconium-iso-propoxide have been decomposed by microwaves to form secondary precursors for the preparation of composites [19].

Direct pyrolysis of metal organics by conventional heating is unsuitable for powder production because it gives rise to nonuniform powder morphology. Several other technological problems have been reported to be associated with combustion methods [20]. However, when metal-organic liquids are subjected to microwave irradiation, very rapid and volumetric heating occurs, which leads to their decomposition. This is expected to result in the formation of products of good structural and, eventually, of morphological uniformity. Microwave pyrolysis is superior to conventional heating since, in most instances, it behaves as a self-regulating process (microwave absorption characteristics change drastically once the susceptor is either chemically or physically altered) and, therefore, products having uniform particle size distribution can be expected to form. Different precursors in a mixture exhibit different susceptibilities and, therefore, lead to different thermal histories at a microscopic level. This can be exploited in the preparation of ceramic composites with unique morphologies.

Very little is known in the literature with regard to the use of microwaves in the preparation of ceramic powders and composites starting from organic precursors. In this paper we report our investigations on the use of organic precursors in the microwave-assisted preparation and sintering of mullite and mullite-zirconia composites.

Another important aspect of this work is our investigation into microwave-assisted sintering of mullite and mullite-zirconia composites. Pure mullite is difficult to densify at temperatures below 1973 K, due to the slowness of diffusion of aluminum and silicon in the product [21]. However, it is well known that the addition of ZrO<sub>2</sub> promotes densification and retards grain growth of the mullite phase [22]. Different processing routes for obtaining mullite-zirconia ceramics of high densities have been reported in the literature, such procedures were reviewed in 1994 by Schneider *et al.* [1].

Mullite and mullite-zirconia mixtures are generally microwave inert at low temperatures, but they have been found to sinter rapidly in microwaves when irradiated at higher temperatures. Higher temperatures are achieved by a technique based on using a secondary heater in the microwave field [18]. In this “hitch-hiking” approach, materials which are inert to microwaves at low temperatures are embedded in another, strongly microwave-active material (secondary heater) and then subjected to microwave irradiation. The critical requirement is that the material of the secondary heater be chemically unreactive with the material being sintered [18].

## EXPERIMENTAL DETAILS

For the microwave heating experiment, we employed a microwave oven (Batliboy Eddy, India) operating at a frequency of 2.45 GHz and maximum output power of 980 W. We selected, as the organic precursors, aluminum-tri-sec butoxide (C<sub>4</sub>H<sub>9</sub>O)<sub>3</sub>Al, tetraethyl orthosilicate (C<sub>2</sub>H<sub>5</sub>O)<sub>4</sub>Si (TEOS), and zirconium-iso-propoxide (C<sub>3</sub>H<sub>7</sub>O)<sub>4</sub>Zr. For the preparation of mullite, a calculated quantity of aluminum-tri-sec butoxide and TEOS were mixed with

TABLE 1  
Microwave Preparation Conditions and the Compounds Formed

Starting material	Microwave power (W)	Exposure duration (min)	Compound formed
$(\text{C}_4\text{H}_9\text{O})_3\cdot\text{Al}$	560	28	$\text{Al}_2\text{O}_3$ (A)
$(\text{C}_3\text{H}_7\text{O})_4\cdot\text{Zr}$	560	14	$\text{ZrO}_2$ (Z)
$(\text{C}_4\text{H}_9\text{O})_3\cdot\text{Al} + (\text{C}_2\text{H}_5\text{O})_4\text{Si} + \text{CH}_3\text{COOC}_2\text{H}_5$	560	30	$3\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ (M)
$(\text{C}_4\text{H}_9\text{O})_3\cdot\text{Al} + (\text{C}_2\text{H}_5\text{O})_4\text{Si} + (\text{C}_3\text{H}_7\text{O})_4\cdot\text{Zr} + \text{CH}_3\text{COOC}_2\text{H}_5$	560	30	$(3\text{Al}_2\text{O}_3\cdot 2\text{SiO})\cdot\text{ZrO}_2^a$ (MZ)

<sup>a</sup>Four samples were prepared with different proportions of zirconia (up to 40 mol%, in steps of 10 mol%).

ethyl acetate to obtain a clear solution. For the preparation of mullite–zirconia composites, calculated quantities of zirconium-iso-propoxide were added to the ethyl acetate solution containing aluminum-tri-sec butoxide and TEOS. These mixtures were put into glass beakers and irradiated with microwaves for 15 min. Within a few minutes of initiating irradiation, a rapid increase in the viscosity of the metal-organic precursors was observed, and foam-like products were found to form in the beaker within a short duration of further irradiation. At this stage, the microwave oven was switched off and the foam-like powder was removed by gently tapping the beaker. To understand the decomposition characteristics of the precursor components, they were also individually decomposed by microwave pyrolysis. TEOS could not be pyrolyzed directly by microwaves because of its high volatility. Hence, TEOS solution was pre-polymerized by adding water. The experimental details of the microwave pyrolysis are given in Table 1.

Powders obtained from the microwave pyrolysis were characterized using X-ray diffraction (XRD) studies (Jeol), thermogravimetric analysis (TGA), and differential thermal analysis (DTA; Cahn Instruments), Fourier transform infrared spectroscopy (Biorad). Powders were heated in a furnace (Thermolyne 46100) to various temperatures and then examined by X-ray diffraction.

Sintering of mullite and mullite–zirconia composites was performed in the same microwave oven. For the sintering experiments, mullite and mullite–zirconia composite powders were first pelletized under  $196 \text{ MN/m}^2$  pressure to obtain 10 mm diameter pellets of 3 to 5 mm thickness. Polyvinyl alcohol (1%) was used as a binder. The pellets were embedded in  $\beta$ -SiC powders in a silica crucible (about 10 g of  $\beta$ -SiC was sufficient) and the crucible was kept inside the microwave oven. With this set-up, about 25 min was required for complete sintering of the pellets. The products were examined by transmission electron microscopy (TEM; Jeol 200CX) and scanning electron microscopy (SEM; Cambridge Instruments, Stereoscan 360).

## RESULTS AND DISCUSSION

**Microwave-Assisted Preparation.** We designated as the mullite first stage (MF) the decomposition product obtained from the mixture of aluminum-tri-sec butoxide and TEOS in ethyl acetate solution by microwave irradiation after 15 min. MF is a foam-like powder. Figure 1 shows the combined DTA and TGA of MF. From TGA data we note that a large

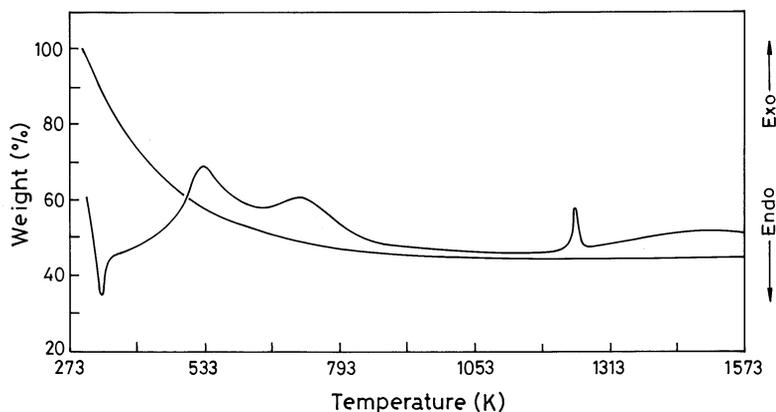


FIG. 1

Combined TGA and DTA plots for microwave-obtained (MF) powder.

weight loss (55%) occurred before 793 K. The DTA for the product exhibits a sharp exothermic peak at 1248 K, which is associated with crystallization of mullite. The XRD pattern (Fig. 2) shows that the microwave-decomposed powder (MF) is amorphous. Heating to a temperature of about 1273 K resulted in a sharp and complete crystallization of mullite. Heating above 1773 K produced very few changes in the XRD patterns. No other phases, such as aluminosilicate spinel,  $\alpha$ -alumina, or cristobalite, were detected in the calcined samples at any temperature.

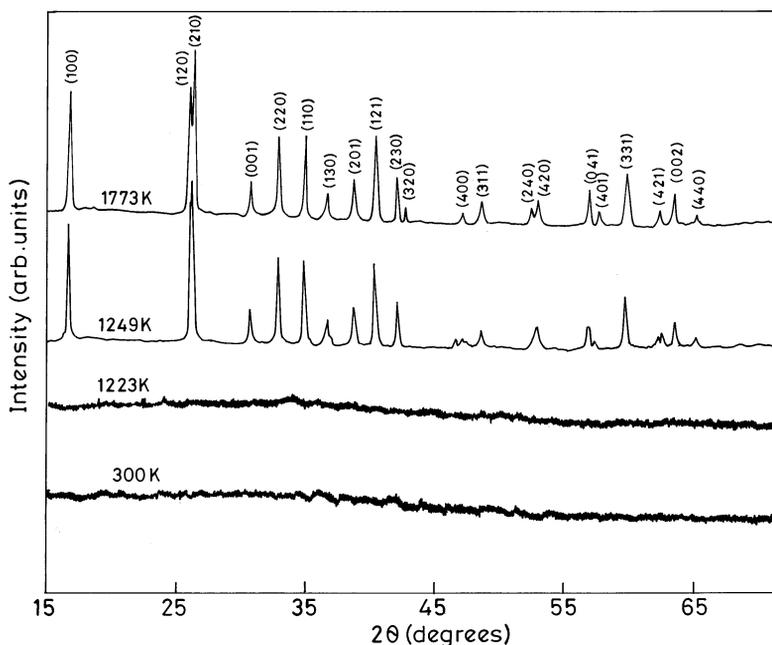


FIG. 2

X-ray diffractogram of MF calcined at various temperatures.

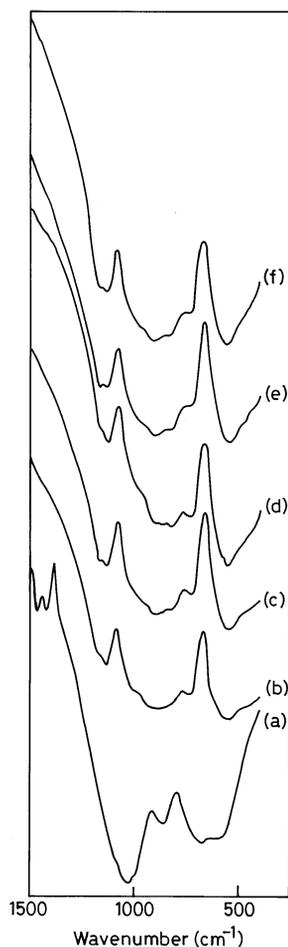


FIG. 3

IR spectra of MF powder calcined at (a) 300 K, (b) 1249 K, (c) 1473 K, (d) 1573 K, (e) 1673 K, and (f) 1773 K.

There have been several reports on the preparation of mullite starting from aluminum and silicon alkoxides [5,7,21,22]. DTA of these products exhibited a sharp exothermic peak at  $\cong 1273$  K. However, XRD patterns of the phases after the exothermic peaks indicated the presence of a small amount of aluminosilicate spinel phase along with mullite. It is well known that the crystallization behavior of mullite precursor depends on the scale of chemical homogeneity of Al and Si atoms [23,24]. When the scale of chemical homogeneity of the precursor is in the nanometer or higher range (diphasic gel),  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  crystallize before mullite formation [25]. On the other hand, mullite crystallizes directly at about 1273 K from the precursors if there is atomic-scale mixing of Al and Si atoms in them [4,26,27]. Since the present product exhibited a sharp exothermic peak at about 1273 K, due to crystallization of mullite, the chemical homogeneity of MF can be regarded as high and of atomic scale.

Figure 3 shows the IR spectra of microwave-obtained mullite powder heat-treated at

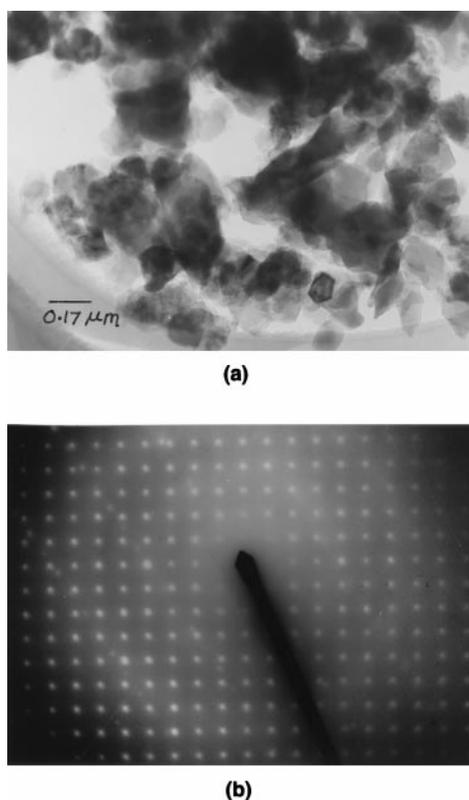


FIG. 4

(a) TEM image of MF calcined at 1773 K for 3 h and (b) corresponding electron diffraction pattern projected from (001).

different temperatures. The spectra of as-produced amorphous powders are different from those of amorphous  $\text{SiO}_2$  powders and bohemite gel [4]. There is a recognizable similarity between the spectra of amorphous powder and the crystallized mullite (1273 K). For example, in Figure 3 the broad peak in the region of  $600\text{ cm}^{-1}$  and the sharp peak at  $1010\text{ cm}^{-1}$  can be correlated with  $550$  and  $1150\text{ cm}^{-1}$  peaks in crystallized mullite. Therefore, the as-produced mullite powders are unlikely to be simple mixtures of  $\text{SiO}_2$  and aluminum hydroxide. They seem to be already close to the chemistry of mullite. Therefore, Si–O–Al bonding has already occurred in the structure. The absorption band at  $1041\text{ cm}^{-1}$  in the IR spectrum of the as-produced powder corresponds to  $\nu_{\text{Si-O}}$  red-shifted absorption at  $1100\text{ cm}^{-1}$  normally present in the spectrum of  $\text{SiO}_2$ . The lowering of the frequency results from the introduction of Si–O–Al bonds [4] in place of stiffer Si–O–Si bonds. Structural changes occurring in the particles during heating can be characterized by shifts of the  $\nu_{\text{Si-O}}$  band. The absorption band in the  $500$  to  $800\text{ cm}^{-1}$  region is associated with both octahedral and tetrahedral Al–O bonds; this agrees well with the calculated data on ideal mullite [28].

Figure 4 shows the TEM image (a) and the corresponding diffraction pattern (b) of mullite powders heat-treated at 1773 K for 3 h. This pattern confirms the completion of mullite formation and of the faceted submicron-size crystallites. The  $d$  values calculated from

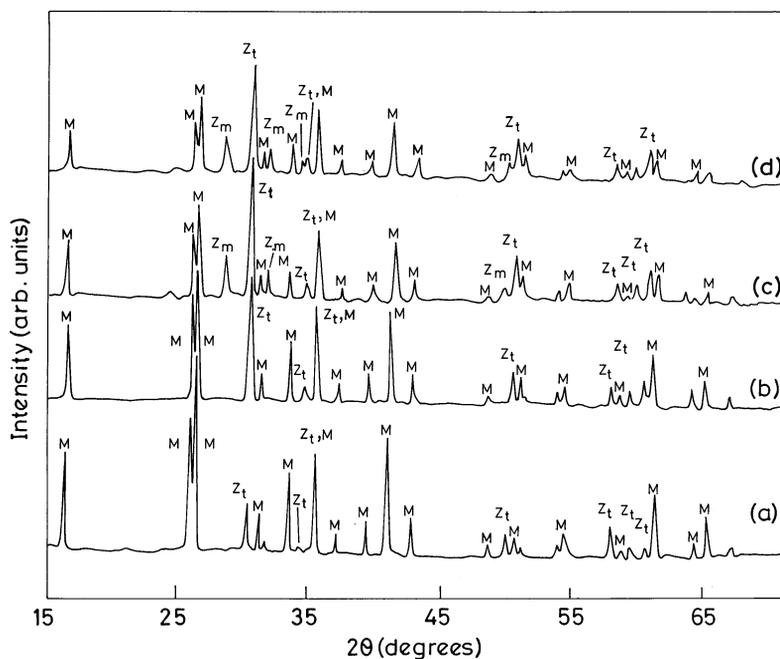


FIG. 5

X-ray diffractograms of microwave-obtained mullite–zirconia powders heat-treated at 1773 K for 3 h: (a)  $MZ_1$ , (b)  $MZ_2$ , (c)  $MZ_3$ , and (d)  $MZ_4$  (see Table 1 for definition of  $MZ_1$ ,  $MZ_2$ ,  $MZ_3$ , and  $MZ_4$ ). M = mullite;  $Z_m$  = monoclinic  $ZrO_2$ ;  $Z_t$  = tetragonal  $ZrO_2$ .

electron microscopy ( $d_{100} = 7.6 \text{ \AA}$ ;  $d_{010} = 7.7 \text{ \AA}$  and  $d_{001} = 2.9 \text{ \AA}$ ) agree well with the XRD values obtained in the present work and from the literature [31,32].

Mullite–zirconia composites were obtained by the microwave decomposition of mixtures of ASB, TEOS, and zirconium-iso-propoxide in ethyl acetate solution. This process yielded a foam-like powder designated as mullite–zirconia foam (MZF). XRD results show that these powders were amorphous. The foam-like powder was used as a second-stage precursor for the preparation of mullite–zirconia composites. On calcination at 1773 K in a conventional

TABLE 2  
Sintering of Mullite and Mullite-Zirconia Composites by Use of Microwave Irradiation

Sample	Composition	Microwave power (W)	Sintering duration (min)	Temp. (K)	Green density ( $\text{g/cm}^3$ )	Sintered density ( $\text{g/cm}^3$ )	Relative density (%)
M	Mullite	980	35	1733	1.82	2.95	92
MC <sup>a</sup>	Mullite	-	-	-	1.82	3.00	94
$MZ_1$	90M + 10 $ZrO_2$	980	35	1733	1.94	3.21	96
$MZ_2$	80M + 20 $ZrO_2$	980	35	1733	2.05	3.38	96
$MZ_3$	70M + 30 $ZrO_2$	980	35	1733	2.15	3.59	97
$MZ_4$	60M + 40 $ZrO_2$	980	35	1733	2.27	3.37	95

<sup>a</sup>Mullite sintered at 1723 K for 5 h in a conventional furnace.

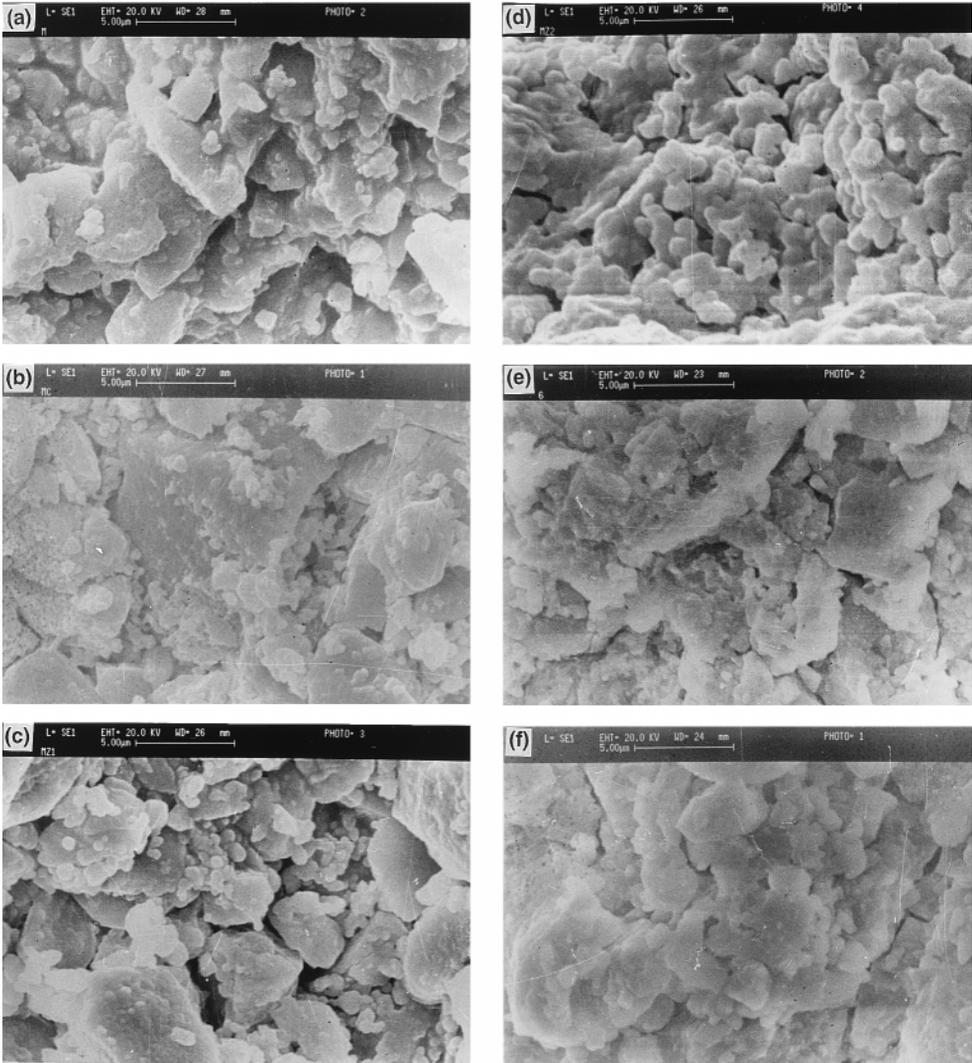


FIG. 6

SEM images of freshly fractured surfaces of microwave-sintered pellets: (a) M, (b) MC, (c) MZ<sub>1</sub>, (d) MZ<sub>2</sub>, (e) MZ<sub>3</sub>, and (f) MZ<sub>4</sub>.

furnace, MZF powders gave rise to mullite–zirconia composites. Four mullite–zirconia composites were prepared with different percentage of zirconia (10–40 mol%). Figure 5 shows the XRD patterns of MZF powders containing different percentages of ZrO<sub>2</sub> heat-treated to 1773 K for 3 h. In all these composites, zirconia was found to be present mostly in the tetragonal phase. In ZrO<sub>2</sub>-rich composites, there is also weak but definite evidence of the presence of monoclinic ZrO<sub>2</sub>, and the peak is indicated in Figure 5c and d. Such a tendency for ZrO<sub>2</sub> to transform into monoclinic phase in mullitic phases has been reported [30].

**Microwave-Assisted Sintering.**  $\beta$ -SiC used as a secondary heater initially reached a temperature of about 1073 K. As a consequence, the temperature of the pellets increased to nearly 1000 K. Once the pellets were heated to this temperature, direct microwave absorption by the pellets became significant. The direct coupling of the mullite–zirconia ceramics to microwaves escalated the temperatures to 1773 K. Efforts to measure the temperature profile continuously during sintering were unsuccessful, since the thermocouple could not be kept inserted in the  $\beta$ -SiC cover during sintering. Only the microwave power of the oven was kept constant during sintering. Temperatures of the pellets, however, were measured at various stages, by pushing a thermocouple (Pt–Pt 13% Rh) to the surface of the pellets while the microwave power was briefly switched off. The pellets attained their maximum temperatures in approximately 15 min of exposure and these temperatures were recorded. The densities of the pellets were measured after 35 min of sintering operation.

Pure mullite could be sintered to only 92% of theoretical density. When the same mullite pellets were sintered at 1723 K in a conventional furnace for 5 h for comparison, they were found to sinter to a density of 94%. The effect of adding zirconia on the microwave sintering was evident in the final densities of the composites. All mullite–zirconia composites were found to sinter to still higher densities for the same duration of 35 min of sintering. The sample with 40% of zirconia sintered to a maximum of 97% of theoretical density. Microwave power, duration of irradiation, and final densities of the products in these experiments are summarized in the Table 2.

The sintered samples were examined using SEM. The micrographs of the fractured surfaces of the pellets are shown in Figure 6. The microstructure of pure mullite (M) appears flaky. But, in  $MZ_4$  the particles are round and smooth in appearance. A similar appearance of particles was noticed when alumina and zirconia powders bounded by PVA were sintered by conventional heating, but the densities produced by sintering were remarkably low [33]. The microstructures of  $MZ_1$ ,  $MZ_2$ , and  $MZ_3$  were intermediate in appearance. Also particles were larger in size in sintered M, compared to those in  $MZ_4$  and other samples. Larger particle size has the effect of slightly increasing the enclosed porosity (see densities in Table 2): that of M is larger than that of the composites. But there was no clear distinction in particle contrasts in the micrographs, i.e.,  $ZrO_2$  particles could not be distinguished from those of  $Al_2O_3$ .

## CONCLUSIONS

Mullite and mullite–zirconia composites were prepared by a microwave-assisted method starting from metal-organic liquids. This method involves preparation of second-stage precursors, which are later heated in a conventional furnace to decompose and crystallize the products. The products are sintered by microwave heating to high densities.  $ZrO_2$  is retained largely in tetragonal form in the composites.

## REFERENCES

1. H. Schneider, K. Okada, and J. Pask, in *Mullite and Mullite Ceramics*, ed. K. Okada, p. 146, John Wiley and Sons. Ltd., Chichester, UK (1994).
2. H. Schneider, B. Saruahan, L. Merwin, and A. Sebald, *J. Eur. Ceram. Soc.* **11**, 87 (1993).
3. K. Okada and N. Otsuka, *J. Am Ceram. Soc.* **69**, 652, (1986).

4. Y. Hirata, K. Sakeda, Y. Matsushits, K. Shimada, and Y. Ishihara, *J. Am. Ceram. Soc.* **72**, 995 (1989).
5. O. Sakurai, N. Mizutani, and M. Kato, *J. Ceram. Soc. Jpn.* **96**, 639 (1988).
6. S. Hori and R. Kurita, *Ceram. Trans.* **6**, 311 (1990).
7. M. Inoue, H. Kominami, and T. Inui, *J. Am. Ceram. Soc.* **79**, 792 (1996).
8. D.R. Baghurst and D.M.P. Mingos, *J. Chem. Soc., Chem. Commun.*, 829 (1988).
9. W.H. Sutton, *Am. Ceram. Soc. Bull.* **68**, 376 (1989).
10. C.C. Landry and A.R. Barron, *Science* **260**, 1653 (1993).
11. S. Komarneni, E. Breval, and R. Roy, in *Microwave Processing of Materials*, ed. W.H. Sutton, M.H. Brooks, and I.J. Chabinsky, Vol. 124, p. 235, Materials Research Society, Pittsburgh, PA (1988).
12. T.T. Meek, C.E. Holcombe, and N. Dykes, *J. Mater. Sci. Lett.* **6**, 1060 (1987).
13. K.J. Rao and P.D. Ramesh, *Bull. Mater. Sci.* **18**, 447 (1995).
14. M. Willert-Porada, *MRS Bull.* **18**, 51 (1993).
15. P.D. Ramesh, B. Vaidhyanathan, M. Ganguli, and K.J. Rao, *J. Mater. Res.* **9**, 3025 (1994).
16. P.D. Ramesh, and K.J. Rao, *Adv. Mater.* **7**, 177 (1993).
17. B. Vaidhyanathan, M. Ganguli, and K.J. Rao, *J. Mater. Chem.* **6**, 391 (1996).
18. P.D. Ramesh, P. Sarin, S. Jeevan, and K.J. Rao, *J. Mater. Synth. Processing* **4**, 163 (1996).
19. B.G. Ravi, P.D. Ramesh, N. Gupta, and K.J. Rao, *J. Mater. Chem.* **7**, 2043 (1997).
20. D.W. Sproson, G.L. Messing, and T.J. Gardner, *Ceram. Int.* **12**, 3 (1986).
21. M.D. Sacks and J.A. Pask, *J. Am Ceram. Soc.* **65**, 65 (1982).
22. H. Suzuki and H. Saito, *J. Mater. Sci.* **25**, 2253 (1990).
23. S. Prochazka and F.J. Klug, *J. Am. Ceram. Soc.* **66**, 874 (1983).
24. B.E. Yoldas, in *Mullite and Mullite Matrix Composites*, ed. S. Somiya, R.F. Davis, and J.K. Pask, Vol. 6, pp. 225, American Ceramic Society, Westerville, OH (1990).
25. K. Okada, N. Otsuka, and S. Somiya, *Am. Ceram. Soc. Bull.* **70**, 1633 (1991).
26. I.A. Aksay, D.M. Dabbs, and M. Sarikaya, *J. Am Ceram. Soc.* **74**, 2343 (1991).
27. K. Okada and N. Otsuka, *J. Am. Ceram. Soc.* **69**, 652 (1986).
28. J.A. Pask, X.W. Zhang, A.P. Tomsia, and B.E. Yoldas, *J. Am. Ceram. Soc.* **70**, 704 (1987).
29. J.C. Huling and G.L. Messing, *J. Am. Ceram. Soc.* **74**, 2374 (1991).
30. K.J.D. Mackenzie, *J. Am. Ceram. Soc.* **55**, 68 (1972).
31. M.D. Sacks, N. Bozkurt, and G.W. Scheiffer, *J. Am. Ceram. Soc.* **74**, 2428 (1991).
32. W.E. Cameron, *Am. Ceram. Soc. Bull.* **56**, 1003 (1977).
33. R. Misra and K.J. Rao, *Ceram. Int.*, in press.