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Mullite from clay–reactive alumina for insulating substrate application

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Abstract

Clay-based mullite was prepared for insulating substrate applications. The clay and reactive alumina are the starting materials for the stoichiometric mullite prepared by reaction sintering at 1600 °C/3 h. MgO and boehmite were added as sintering aid to improve the density and decrease the sintering temperature. The properties of the sintered bodies, such as thermal, electrical and mechanical properties of the sintered samples were studied. The boehmite (5.0 wt.%) substituted for reactive alumina mixture showed higher density (96% theoretical density). Clay and reactive alumina completely reacted at 1600 °C and formed mullite phase. Samples with 3.0 wt.% MgO addition showed the presence of secondary phases such as α-alumina and spinel. The mullite crystals formed are needle-shaped with rectangular faces. The MgO (3.0 wt.%) addition slightly decreased the thermal expansion. Dielectric constant values are almost same for the samples with boehmite or MgO addition.
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1. Introduction

Mullite is not only having good high temperature properties but also excellent electrical insulating ability making it potentially useful in applications ranging from refractories to electronic substrates (Ebadzadeh and Lee, 1998). Ceramic substrates have played an important role in high performance electronic products. In recent years, the logic devices with higher integration density, higher signal propagation rate, low dielectric constant and low thermal expansion coefficient have been developed (Somiya and Hirata, 1991; Kansaki et al., 1990). In high density packaging, the important requirements are (1) thermal expansion match with silicon in order to reduce the thermal stresses, (2) low dielectric constant to enhance signal processing and (3) high thermal conductivity for heat dissipation from the hard-driven integrated circuit devices (Schneider, 1991).

Traditionally, alumina ceramics dominate this area of application for their outstanding thermal and corrosion stability. However, the high dielectric constant

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and high thermal expansion coefficient of alumina cause delay in signal propagation and thermal expansion mismatch between substrate and silicon chip, respectively (Kansaki et al., 1990). As a substrate, chemically pure mullite with a dielectric constant about 6.7 results in about 17% lower signal transmission delay time than alumina. In addition, mullite has a low-thermal expansion coefficient (4×10^{-6}/°C in the 20–200 °C range), which is almost comparable to that of silicon (3.5×10^{-6}/°C) (Aksay et al., 1991). Although a number of papers have been published with regard to the application of mullite ceramics for substrate, most of them used the mullite synthesized from different raw materials but not from clay (Ebadzadeh and Lee, 1998; Goski and Caley, 1999; Kansaki et al., 1990; Tummala, 1991).

When alumino-silicate minerals are heated above 1400 °C, they react to form primary mullite and SiO_2. The reaction of kaolinite with alumina is of interest in the production of mullite reaction sintering (Liu and Thomas, 1994). At a temperature above 1400 °C, secondary mullite formation takes place by dissolution of alumina into transitory liquid phase, followed by the precipitation of mullite crystals (Rezaie et al., 1997). The rate of secondary mullite formation is very slow till the eutectic liquid formation at 1587 °C and extremely fast at 1600 °C (Liu and Thomas, 1994).

Mullite powder compacts have poor solid state sinterability because of the low interdiffusion rates of Si^{4+} and Al^{3+} within the mullite lattice (Lee and Rainforth, 1994). On the other hand, the kinetics of forming mullite by the action of MgO (Amutharani, 1998; Ismail et al., 1990; Montanaro et al., 1997, 2000) and boehmite (Amutharani, 1998; Viswabaskaran, 2002) was well proved. These additives aid in sintering of mullite and so sintering can be carried out
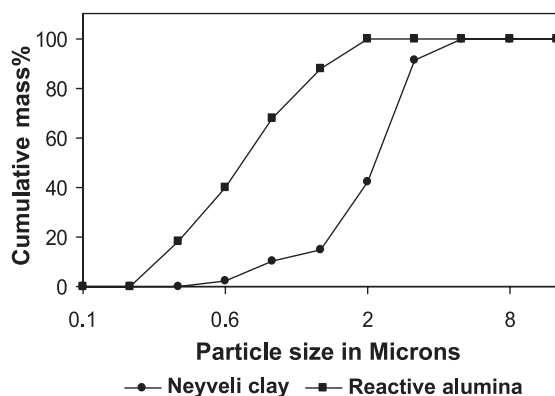

Fig. 1. Particle size distribution of clay and reactive alumina.

at a relatively low temperature. The study reported in this paper compared the effect of MgO and boehmite on the sintering of kaolinite-reactive alumina mixture. As a kaolinite source, the Neyveli clay is the best source available in India and the mullitisation of this clay is also best among the Indian clays (Viswabaskaran et al., 2002a). X-ray diffraction (XRD) and microstructural studies were carried out to understand the mullitisation. The porosity, bulk density and bending strength of the samples were determined. The dielectric constant and coefficient of thermal expansion were also measured.

2. Experimental

Experiments were carried out with raw kaolinite clay from Neyveli, India and reactive alumina (SG 9000 mean grain size 0.7 μm). As per the stoichiometric composition (72 wt.% of Al_2O_3), the materials are carefully weighed before milling. Our work (Viswabaskaran, 2002) revealed that 3.0 wt.% MgO addition and 5.0 wt.% boehmite, synthesized from aluminium isopropoxide (Sathyakumar, 2000), substitution with the above composition resulted in the maximum density and flexural strength. The same amount of MgO (3.0 wt.%) was added for making the sample batches. A total of 5.0 wt.% boehmite is added as a substitute for the reactive alumina. The various batches are carefully wet milled for half an hour in a planetary mill using alumina milling medium for thorough mixing. Finally, slurries were dried at 100 °C for 72 h. Rectangular bars ($5 \times 5 \times 50$ mm³) and

Table 1
Chemical analysis of raw materials (wt.%)

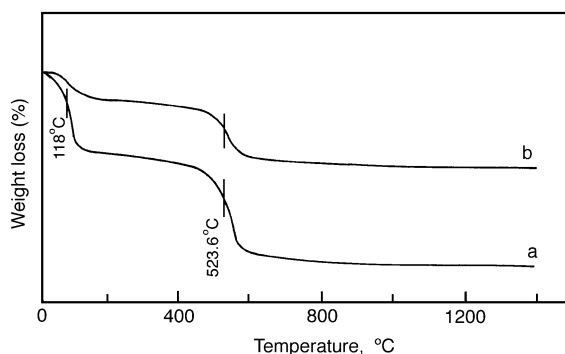| Elements	Neyveli clay	α-Alumina
SiO_2	43.26	0.01
Al_2O_3	36.11	99.85
Fe_2O_3	1.06	0.02
TiO_2	1.59	–
CaO	0.37	0.01
MgO	1.40	–
Na_2O	0.11	0.08
K_2O	0.10	–
LOI	16.00	–

Fig. 2. Thermogravimetric analysis of (a) Neyveli clay and (b) clay-reactive alumina mixture.

discs of 9–10 mm diameter and ≈ 1 mm thickness were produced by uniaxial pressing of powders in a steel die at 200 MPa and were sintered in an electric furnace at a heating rate of 5 °C min⁻¹ in air to 1600 °C and held 3 h before furnace cooling.

Particle size distribution analysis was carried out for the starting raw materials using Shimadzu laser particle size analyzer model SALD 1100. Powders were characterized by differential thermal analysis (DTA) and thermogravimetric analysis (TG) using NETZSCH STA409PC with α-alumina as the refer-
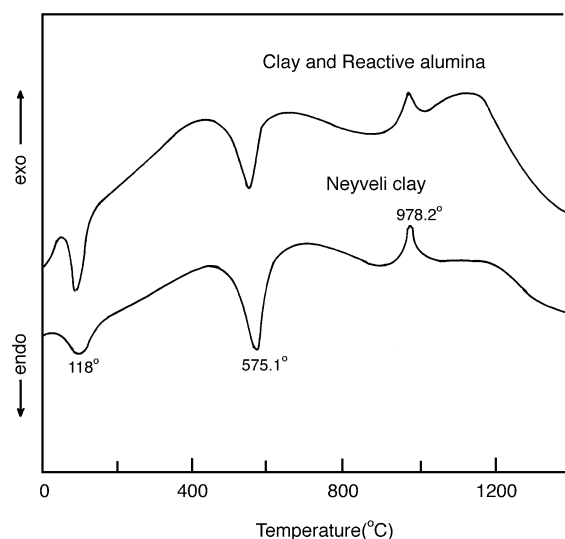
ence material at a heating rate of 5 °C min⁻¹ in air. The powder samples were passed through − 200 ASTM mesh size and were dried at 110 °C for 2 h before thermal analysis. The phases present in the sintered specimens were identified by XRD technique using Siemens D-500 powder diffractometer using Cu K_α radiation. The bulk density of the pellets was measured by Archimedes principle. Modulus of rupture (MOR) was determined on rectangular samples fired at 1600 °C/3 h using universal testing machine (Zwick 1445). Dielectric constant measurements were made on disc-shaped samples. All measurements were undertaken at room temperature on a Hewlett Packard HP4284A Precision LCR meter, with a frequency range from 1 to 13 MHz. The thermal expansion coefficients of the sintered specimens were measured by a NETZSCH dilatometer at a heating rate of 5 °C min⁻¹. All the samples were polished and thermally

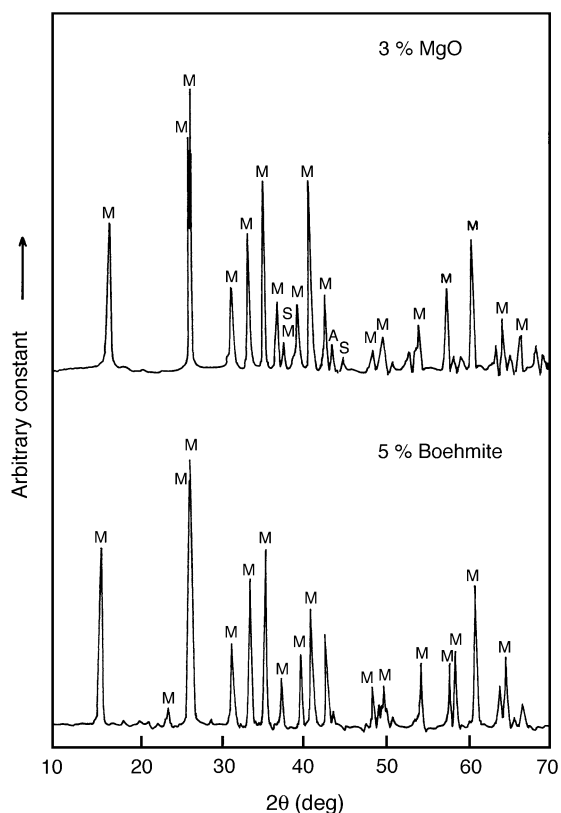Fig. 3. Differential thermal analysis of (a) Neyveli clay and (b) clay-reactive alumina mixture.

Fig. 4. XRD analysis of sintered test samples containing MgO and boehmite.

etched for 1 h at about 100 °C lower than the sintering temperature and subsequently examined in a scanning electron microscope (SEM) using Cambridge Instruments-5526 scanning electron microscope.

3. Results and discussion

Table 1 shows the chemical composition (wt.%) of Neyveli clay and reactive alumina. The clay contains a moderate amount of impurities and is the best available clay source in the state of Tamilnadu, India (Viswabaskaran et al., 2002b), whereas reactive alumina is pure. Reactive alumina is having narrow and fine particle size distribution with mean particle size of 0.7 μm. The Neyveli clay is also having smaller particle size with narrow particle size distribution and the largest size of the particles (d_{100}) is around 6.0 μm (Fig. 1). TG results are shown in Fig. 2. The weight loss occurs at two stages, first
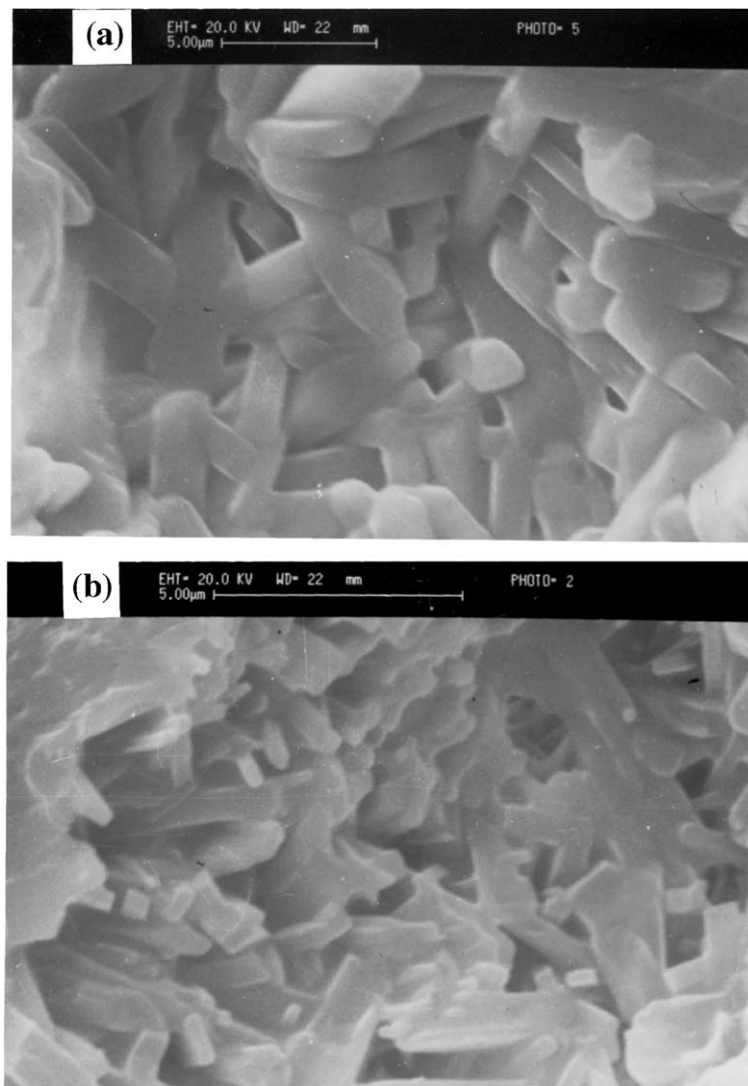

Fig. 5. Microstructure of mullite samples (a) 3.0 wt.% MgO and (b) 5.0 wt.% boehmite.

around 110 °C is due to removal of absorbed water and the second around 550°C is due to removal of structural water from clay. The total weight loss is comparatively lower in the clay–reactive alumina mixture because the water removal is only from clay and not from the reactive alumina. The DTA curves (Fig. 3) for clay and clay–reactive alumina give two endothermic peaks due to loss of absorbed and structural water at 110 and 550 °C, respectively. A prominent exothermic peak at around 980 °C and a much smaller exothermic peak between 1200 and 1250 °C in the derivative curve (not visible in figure) are due to the formation of 2:1 mullite and spinel from meta-kaolin, followed by 3:2 mullite formations (Rezaie et al., 1997). The DTA result shows that the two endothermic peaks are the characteristic peaks of kaolinite clay.

The XRD results of the sintered samples are shown in Fig. 4. It clearly indicates that there is no cristobalite and α-alumina peaks in all samples. This confirms that the reaction of clay and reactive alumina at 1600 °C for 3 h is sufficient to convert to mullite. However, the samples with 3.0 wt.% MgO addition show the presence of secondary phases such as α-alumina and $MgO-Al_2O_3$ spinel. Many authors (Montanaro et al., 1997, 2000) have reported that sinter additives like MgO promote sintering in the presence of liquid phase, which is formed in a very narrow temperature range of 1410–1425 °C. It may be understood from the $MgO-Al_2O_3-SiO_2$ phase diagram (Montanaro et al., 2000) that MgO can produce a Mg–Al spinel at high temperature. However, at temperatures above the peritetectic point (1578 °C for pure system), the equilibrium phases are mullite, α-Al_2O_3 and the liquid. According to the phase diagram, the spinel phase does not exist above the peritetectic point. The Mg–Al spinel crystals may be formed as a result of devitrification of the liquid phase during cooling. The mullite grains grow
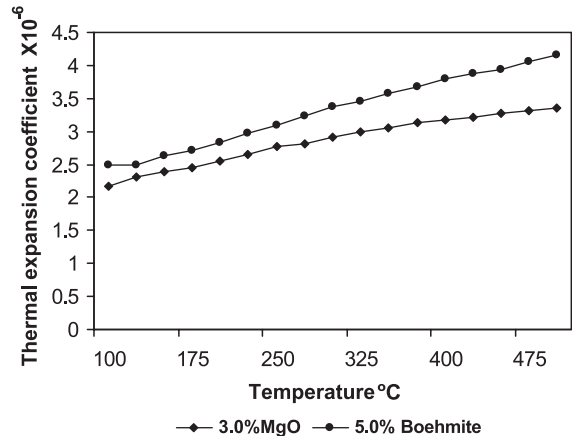

Fig. 6. Thermal expansion of sintered test samples containing MgO and boehmite.

during devitrification, entrapping the spinel precipitates (Montanaro et al., 2000). This may be the reason for the detection of small peaks of α-alumina and $MgO-Al_2O_3$ spinel for samples containing 3% MgO.

The microstructure of the samples sintered at 1600 °C for 3 h is shown Fig. 5. The 3.0 wt.% MgO gives larger grain size and is very closer; the primary mullite crystals are grown to 20 μm in length and 5–6 μm in width (Fig. 5a). Secondary mullite is also present through out the system. It can be observed that mullite crystals are needle-shaped with rectangular faces. By adding MgO, the grain growth is accelerated, leading to the formation of coarser grains (Viswabaskaran, 2002).

Fig. 5b shows the microstructure of boehmite substituted samples. The 5.0 wt.% boehmite substitution gives various sizes of primary and secondary mullite. They are not equal in shape and size and they are 1–15 μm in length and 1–5 μm in width. There is no considerable grain growth observed. The 5.0 wt.% boehmite-containing sample shows minimum pore area and high quantity of mullite. The boehmite addition in the mixture increases the size distribution of mullite grains. This is the reason for the maximum density and low porosity of boehmite substituted samples.

The physical properties of the sintered samples are presented in Table 2. The bulk density of samples with 3.0 wt.% MgO is 2.91 g cm^{-3} and the

Table 2
Physical properties of clay based mullite

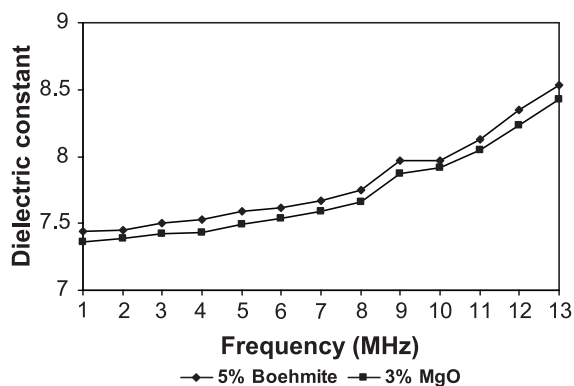| Properties	3% MgO	5% boehmite
Bulk density (g cm^{-3})	2.91	3.01
Flexural strength (MPa)	126 (5)[a]	120 (5)[a]

[a] Standard deviation.

Fig. 7. Dielectric constant of sintered test samples containing MgO and boehmite.

bending strength is 126 MPa. The boehmite substitution to reactive alumina leads to higher bulk density (3.01 g cm^{-3}) compared to MgO-containing samples. This value equals to 96% theoretical density (3.16 g cm^{-3} JCPDS No. 06-0258). But the strength value (120 MPa) is lower than the MgO-containing sample.

The linear thermal expansion coefficient (30–400 °C) of the sintered bodies is shown in Fig. 6. Thermal expansion coefficient of MgO-containing sample is slightly lower than the samples containing boehmite. The difference is higher at higher temperatures. It has been reported by Somiya and Hirata (1991) that the presence of magnesia in mullite leads to the formation of cordierite during the sintering process. However, there is no clear evidence for the presence of cordierite phase in XRD results for the sample containing 3% MgO.

The dielectric constant of the sintered bodies measured at a frequency range of 1–13 MHz for both MgO- and boehmite-containing samples are shown in Fig. 7. The dielectric constant increases for both the samples on increasing the frequency. Both the samples have almost same dielectric constant at any frequency. However, the dielectric constant obtained in the present study is higher than the value for pure mullite (6.9) but lower than the widely used alumina (9.0) substrates (Schneider et al., 1994). The low dielectric constant is advantageous for high speed propagation of signals in an electronic circuit (Kansaki et al., 1990).

4. Conclusion

From the results of this study, the following conclusions are arrived.

1. Boehmite increases the density to 3.01 g cm^{-3} for clay-based mullite compared to MgO that increases only up to 2.91 g cm^{-3}.
2. Addition of MgO increases the grain growth, while boehmite substitution is not favoring the grain growth. However, the presence of boehmite broadens the grain size distribution. This yields maximum density and moderate strength.
3. The MgO-containing samples are lower in density than the boehmite-containing samples; however, the strength is high.
4. The linear thermal expansion coefficient is comparatively lower for sample containing MgO. The dielectric constant values of both the samples are almost same.
5. The linear thermal expansion coefficient and dielectric constant of the clay derived mullite are higher than the pure mullite; however, the value for clay based mullite is far below the values reported for alumina elsewhere.

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