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Preparation of MgO-doped mullite by sol–gel method, powder characteristics and sintering

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Mullite doped with MgO in quantities ranging from 0.01 to 1.5 wt% were prepared by the sol–gel method. The mullitization temperature decreases with increased MgO dopant content. The XRD patterns of the MgO-doped mullite calcined at temperatures up to 1600° C for durations ranging from 1 to 10 h did not show the presence of any other phase except mullite. The IR spectrum shows a broadening of the Al–O absorbance band at 1175 cm^{-1} with MgO content, indicating the solid solution of MgO. Sintering temperature decreases with increased MgO dopant content. The microstructure observed consisted of equiaxed grains. The TEM observation of the microstructure showed the presence of glassy pockets at the triple grain junctions. The thermal coefficient of expansion and dielectric constant were not changed up to 0.75 wt% MgO dopant concentration. The three-point bend strength observed for 0.3 wt% MgO-doped mullite at room temperature was 300 MPa and decreased below 200 MPa at 1400° C.

1. Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is the main crystalline phase in the Al_2O_3–SiO_2 binary system, and extensive research on its phase equilibria [1–4] and on the effect of dopants on its chemical and physical properties [5–6] has been carried out by different workers.

Mullite is mainly used as a refractory material. In preparation of mullite for refractory bricks using natural raw materials, unintentionally added impurities such as Fe_2O_3, TiO_2 and MgO are present, and these impurities affect its physical and chemical properties depending on the concentration. Mullite can incorporate up to about 12.5 wt% Fe_2O_3, 10.0 wt% Cr_2O_3, 4.0 wt% TiO_2 and 13.0 wt% Ga_2O_3, and these oxides enhance the sinterability of mullite [7, 8].

Pure mullite is considered as a suitable material for structural and substrate applications. Recently, different processes have been tried [9–11] to prepare stoichiometric mullite. It is necessary to use temperatures above 1650° C to sinter these mullite powders to a relative density of 95%. The only alternative is to make mullite more sinterable at low temperatures. This could be achieved by adding a dopant or milling the powder to submicrometre sizes. In one of the processes [12], MgO was added in quantities more than 0.5 wt% to mullite to prepare a substrate with low thermal expansion and dielectric constant. Addition of MgO less than 0.5 wt% had no effect on sinterability, thermal or electrical properties.

In the present investigation, the sol–gel method was adopted to achieve a homogeneous dispersion of MgO in mullite, and the effects of MgO on mullitization, sinterability and physical properties were investigated.

2. Experimental procedures

Boehmite (Catapal B, Vista Chemical Co. Ltd, Texas, USA) and colloidal silica (Nihon Silica Co. Ltd, Tokyo, Japan) were used as the sources of alumina and silica, respectively. Boehmite sol, prepared by peptization of boehmite in the presence of HNO_3 acid, was added to colloidal silica dispersion and mixed in a blender for a few minutes. To this aqueous solution, $MgCl_2 \cdot 6H_2O$ was added and mixed. Mullite sols containing MgO in quantities varying from 0.01 to 1.0 wt% were prepared and gelled by keeping at 100° C. The dried gel was ball milled to pass through a 100-mesh sieve. The effects of MgO on mullitization temperature were studied using the DTA method. The XRD method was used to identify the phases present in the calcined powders. The crystallite size of mullite was determined by using SiO_2 as an internal standard and a mullite (3 3 1) peak. The FTIR spectra of powders were obtained by dispersing in KBr and pressing into discs.

Sintering of these powders was carried out using powder compacts isostatically pressed under 2 tons cm^{-2}. The bulk densities of the sintered compacts were determined by the liquid displacement method. The microstructure of the sintered specimens was observed under the scanning electron microscope (SEM) and transmission electron microscope (TEM). Flexural strength was determined by the three-point bend method. The coefficient of thermal expansion and dielectric constant were measured using Al_2O_3 as an internal standard and at 1 MHz, respectively.

3. Results and discussion

3.1. Mullitization of gel

DTA patterns of mullite gels containing 0.01 to 2.0 wt% MgO were taken at a heating rate of 5° C min^{-1} up to 1400° C. The DTA patterns of pure mullite gel and mullite gel containing 0.3 wt% MgO are given in Fig. 1. The endothermic peak at 420° C

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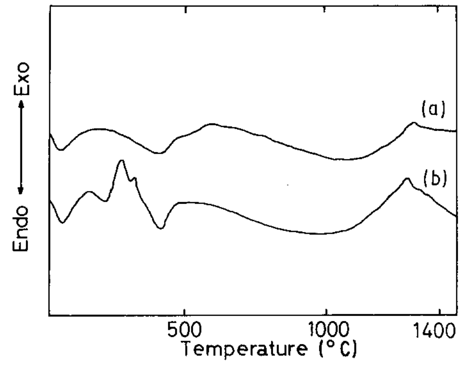


Figure 1 DTA patterns of mullite gel powders (a) without MgO; (b) doped with 0.3 wt % MgO.

indicates the dehydration of boehmite to form γ-Al_2O_3. This was followed by the exothermic peak 1310° C for pure mullite and 1290° C for mullite containing 0.3 wt % MgO.

Variation of mullitization temperature with MgO content is given in Fig. 2. Addition of MgO in quantities more than 0.01 wt % favoured the formation of mullite at a lower temperature. The mullitization temperature decreased with the increase of MgO content up to 1.5 wt % MgO and kept constant above that limit. Mullite gel containing 1.5 wt % MgO crystallizes at 1267° C, which is 43° C lower than the crystallization temperature for pure mullite gel. In earlier studies [13] it was observed that the addition of ZrO_2 favoured the formation of mullite at lower temperatures. Similarly, the presence of MgO lowers the surface free energy of the Al_2O_3–SiO_2 diphasic system and enhances the reactivity, which lowers the crystallization temperature.

3.2. XRD analysis

The XRD patterns of gel containing 0.3 wt % MgO calcined at 1300° C for 1 h are given in Fig. 3. Only peaks corresponding to mullite were observed. Even with an excess of MgO (1.5 wt %) no additional peaks were observed. An increase of MgO content above 2.0 wt % α-cordierite crystallizes with mullite. No peaks corresponding to Mg–Al spinel were observed. The work of Hashimoto and Niwa [12] showed the formation of cordierite even with quantities equal to 0.5 wt % MgO, whereas the sol–gel method allows a nanoscale mixing of Al_2O_3, SiO_2 and MgO and results in a very homogeneous composition. As shown in Fig 3, no cordierite or spinel phase appeared with increased temperature. This shows the formation of solid solution of MgO with mullite.

Variations of the crystallite size of mullite with temperature for compositions containing different proportions of MgO were determined, and are given in Fig. 4. These powders were calcined for 1 h at respective temperatures, and the crystallite size was determined using SiO_2 as an internal standard. As shown in the figure, the crystallite growth was predominant at temperatures above 1400° C and with increased MgO concentration. The crystallite size determined for powders containing up to 0.5 wt % MgO and calcined at 1600° C for 10 h is given in Fig. 5. This figure shows that even with the addition of MgO in the range of 0.01 wt %, a sharp increase of crystallite size with respect to pure mullite was observed. The unit cell volume of the same powders was measured and the variation is given in Fig. 6. As shown in the figure, a slight addition of MgO has caused the unit cell volume of mullite to decrease with respect to pure mullite. But with the increase in MgO content, a slight increase of unit cell volume was observed. The exsolution of MgO with SiO_2 from mullite grains favours the formation of a liquid phase along the grain boundaries, leaving a high alumina mullite matrix phase. This was the reason for the increase of unit cell volume of mullite with MgO content at 1600° C.

3.3. Infrared spectra

The IR spectra of MgO-doped mullite powders calcined at 1600° C for 10 h are given in Fig. 7. For comparison, the IR pattern corresponding to pure mullite is also given. The overall form of the spectra was similar for pure [14] and doped mullite. The characteristic tetrahedral (AlO_4) Al–O vibration at 1175 cm^{-1} broadened with the increased MgO dopant content. The vibration corresponding to Si–O (SiO_4) at 1140 cm^{-1} also increases its intensity with MgO content, whereas the two IR bands corresponding to AlO_4 and SiO_4 vibrations are clearly split for pure mullite. Vibrations corresponding to a magnesium–aluminium spinel (700 to 526 cm^{-1}) [15] were not observed. This clearly shows the formation of solid solution with mullite. The broad peak observed between 820 and 860 cm^{-1} for pure mullite split into

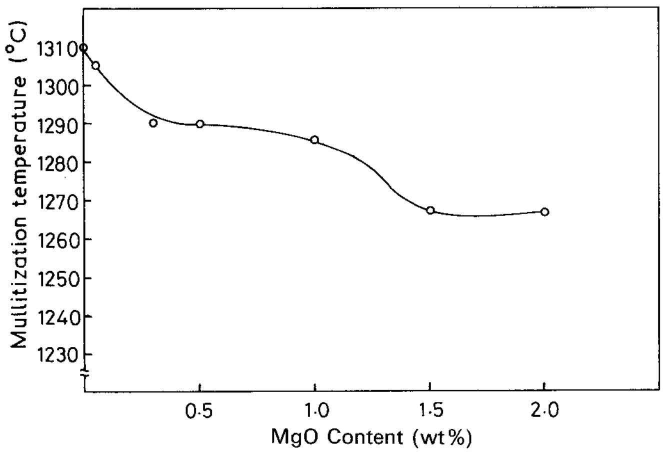


Figure 2 Variation of mullitization temperature with MgO dopant concentration.

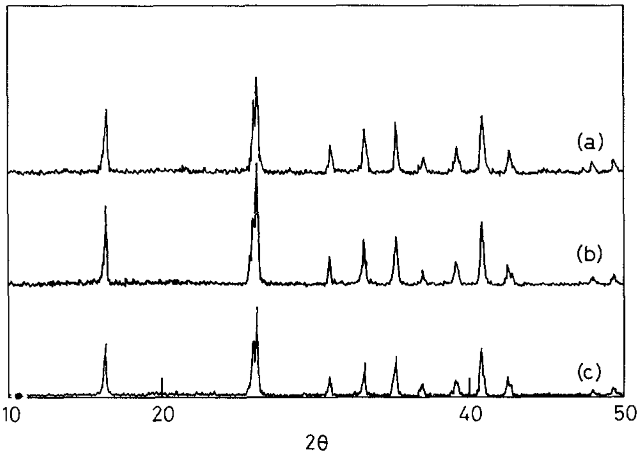


Figure 3 XRD patterns of mullite gel powders containing (a) 0.0, (b) 0.3 and (c) 1.5 wt % MgO calcined at 1300° C for 1 h.

two peaks with increased MgO content. The intensity of the peak at 820 cm^{-1} corresponding to Al–O (AlO$_6$) octahedral vibration increases with increasing MgO content. In the case of pure stoichiometric mullite, this type of transformation was observed only above 1700° C. These results agree well with the unit cell volume data obtained for similar compositions.

3.4. Sintering and microstructure

MgO-doped mullite gel powders were calcined at 1350° C for 1 h and ball milled for 15 h using TZP balls as grinding media. The ball-milled slurry was dried at 100° C and sieved to pass through a 150-mesh sieve. The average particle sizes of the powders are in the range of 1.4 to 1.5 μm. The TEM microphotograph of the mullite powder doped with 0.3 wt % MgO is given in Fig. 8. The morphology of the powder formed does not seem to be influenced by the MgO dopant content. The powders were pressed into rectangular blocks using a uniaxial press and followed by cold isostatic pressing (cip) under 2 tons cm^{-1}. Sintering of these powder compacts was carried out at temperatures between 1450 and 1700° C for durations ranging up to 3 h.

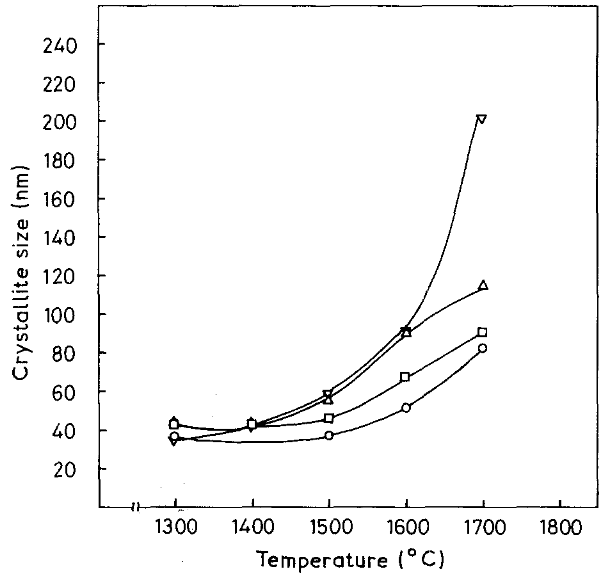


Figure 4 Variation of crystallite size of mullite with temperature for mullite containing different proportions of MgO. ○, Pure mullite; □, 0.05; △, 0.3; ▽, 0.5 wt % MgO.

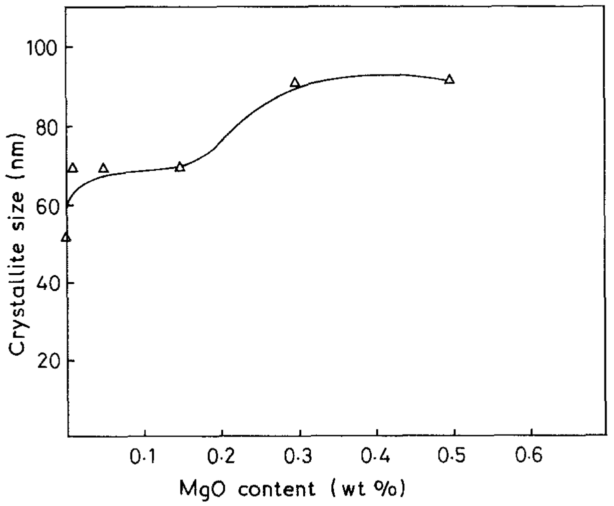


Figure 5 Variation of crystallite size of mullite calcined at 1600° C for 10 h with MgO dopant concentration.

The sintering curves for mullite powders containing 0.01, 0.3 and 0.5 wt % MgO are given in Fig. 9. For pure mullite it is necessary to sinter at temperatures above 1630° C to achieve a relative density greater than 95%. The addition of MgO in quantities more than 0.15 wt % enhance the sinterability of mullite, and could be sintered to > 95% of relative densities at temperatures in the range of 1550° C. The sintered density in all cases increases up to a certain temperature and decreases above this temperature. This is due to the exsolution of SiO$_2$ from mullite grain with increased temperature forming a liquid phase along the grain boundary, and partly vaporizing as SiO. Acicular grains were formed under these conditions and a porous microstructure was obtained; therefore the sintered density decreases.

Figure 10 represents the variation of relative density with MgO content when sintered at 1550° C for 3 h. As shown in this figure, the sinterability of mullite increases with MgO dopant content and decreases above 0.5 wt %. Mullite powder containing MgO above 0.5 wt % has to sinter at temperatures lower than 1550° C to achieve full densification. As discussed

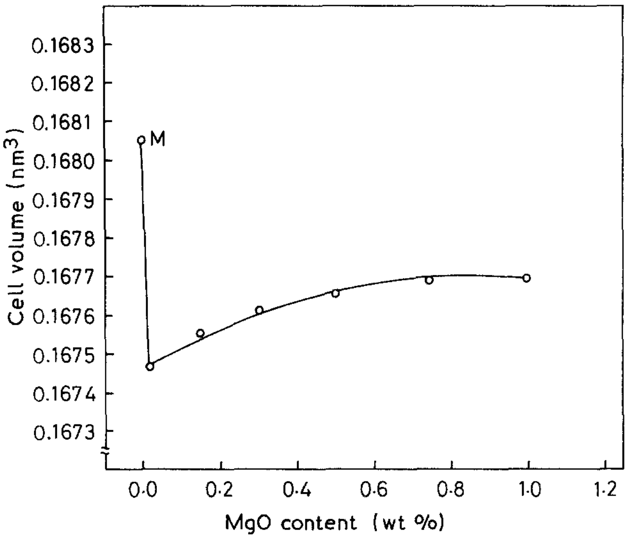


Figure 6 Effect of MgO concentration on the unit cell volume of mullite.

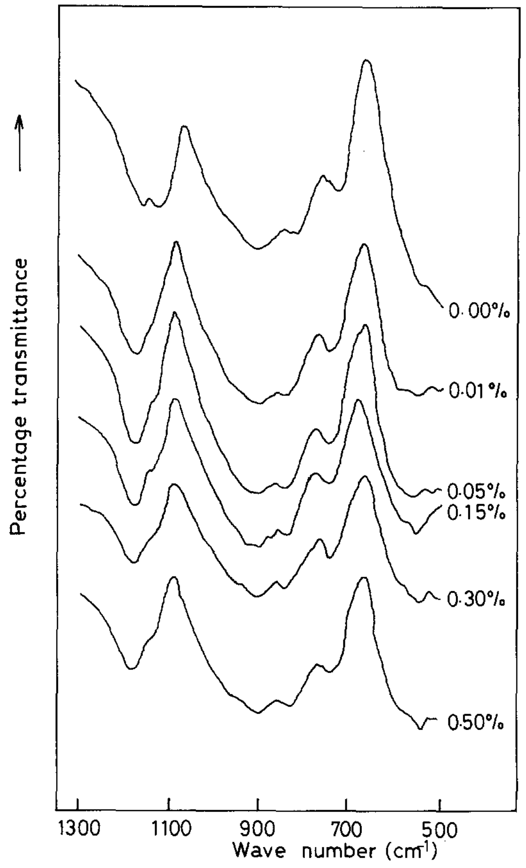


Figure 7 IR spectra of mullite powder containing different proportions of MgO calcined at 1600° C for 10 h.

earlier, increased temperature favours the decomposition of mullite. The decomposition temperature of mullite decreases with increased MgO content. The role MgO in the densification of mullite is not clearly understood. It is well known that MgO accelerates the densification process in alumina by modifying the lattice diffusion coefficient [16]. Similarly in mullite, doping with MgO enhances the densification. It was also observed that MgO favours the formation of translucent mullite at lower temperatures. Vaporization of MgO starts around 1300° C and was predominant at temperatures above 1500° C [17]. Diffusion of MgO and SiO_2 from mullite grains favours the formation of a liquid phase along the grain boundary. This glassy phase modifies the mullite grain morphology from equiaxed to acicular. The overall composition shifts to high-alumina mullite with partial evaporation of MgO and SiO_2 from the glassy boundary layer.

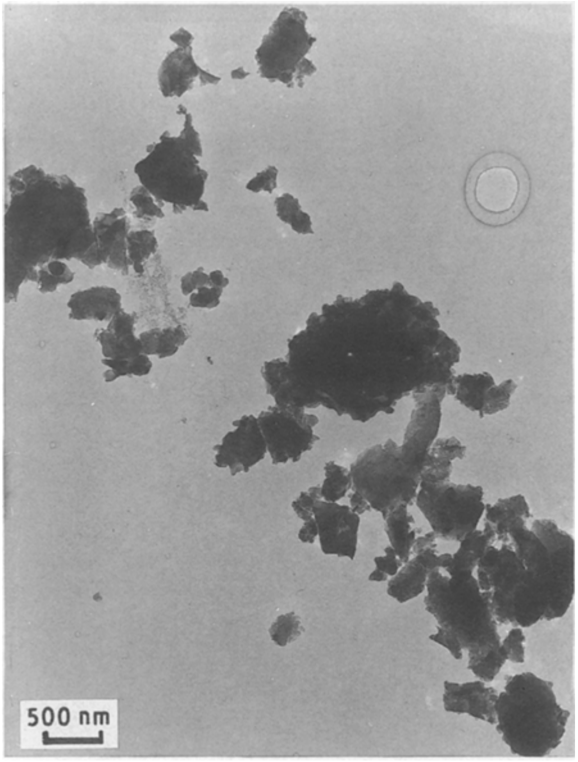


Figure 8 TEM microphotograph of mullite powder containing 0.3 wt % MgO.

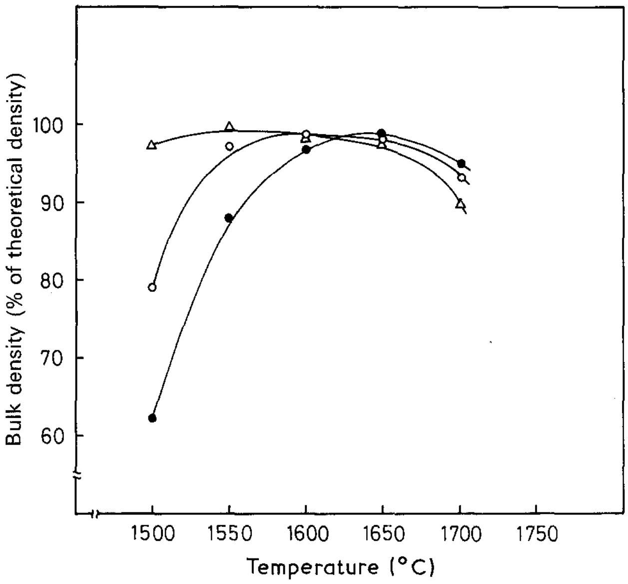


Figure 9 Sintering curves for mullite powder containing different proportions of MgO, ●, 0.01; ○, 0.30; △, 0.50%.

The SEM micrographs of mullite doped with 0.01, 0.30 and 0.75 wt % MgO and sintered at 1640, 1600 and 1550° C for 3 h are given in Fig. 11. SEMs for the same compositions sintered at 1700° C for 3 h are given in Fig. 12; the relative densities achieved by sintering at various temperatures were > 98%, and the grain morphologies were equiaxed. The increase of sintering temperature to 1700° C changed the grain

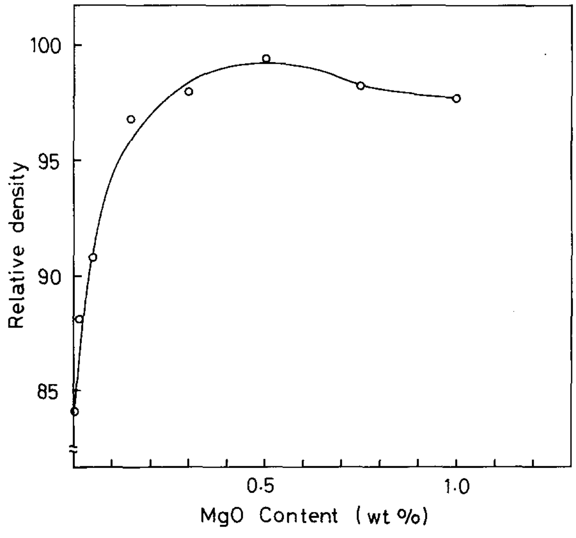
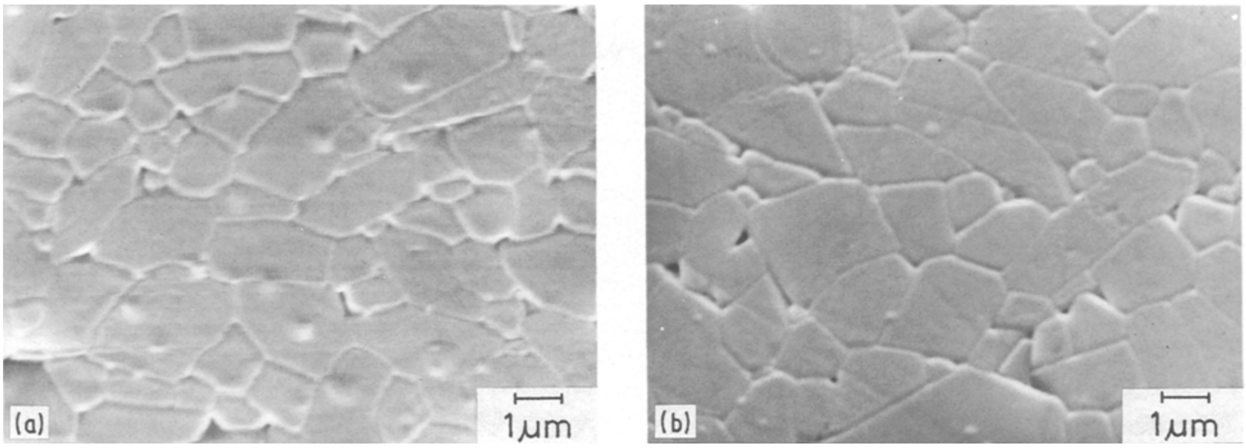


Figure 10 Influence of MgO content on the relative density of mullite sintered at 1550° C for 3 h.



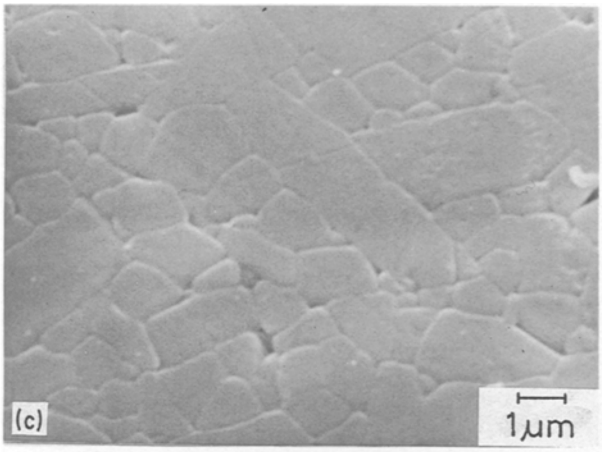


Figure 11 SEM microphotographs of mullite doped with (a) 0.05; (b) 0.30; (c) 0.75 wt % MgO sintered at 1640, 1600 and 1550° C, respectively for 3 h.

morphology to the acicular form with the exsolution of SiO_2 and MgO from matrix phase. The average grain size was determined by the linear intercept method [18] and is plotted against the temperature for mullite containing 0.5 wt % MgO (Fig. 13). A sharp increase in grain size was observed at temperatures above 1600° C. This is in agreement with the data obtained for variation of crystallite size with temperature. As in Al_2O_3, MgO addition has no effect in controlling the grain growth of mullite.

The microstructure observed under the TEM for specimens containing 0.3 wt % MgO and sintered at 1600° C for 3 h is given in Fig. 14. A secondary phase mainly consisting of glassy pockets was observed at the triple-grain corners. The EDS analysis of points within the grain and the glassy pockets showed the presence of Al_2O_3, SiO_2 and MgO. The concentration of MgO within the grain is almost twice that of the secondary phase at the triple point. The presence of Al_2O_3 and SiO_2 with MgO at the triple point as a glassy pocket indicates the dissolution of the mullite grain boundaries by the exsolved MgO from the matrix grain.

3.5. Physical properties

Mullite powders containing MgO dopant concen-

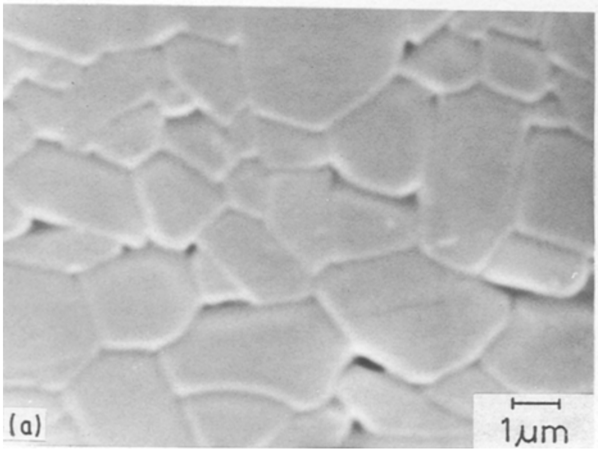
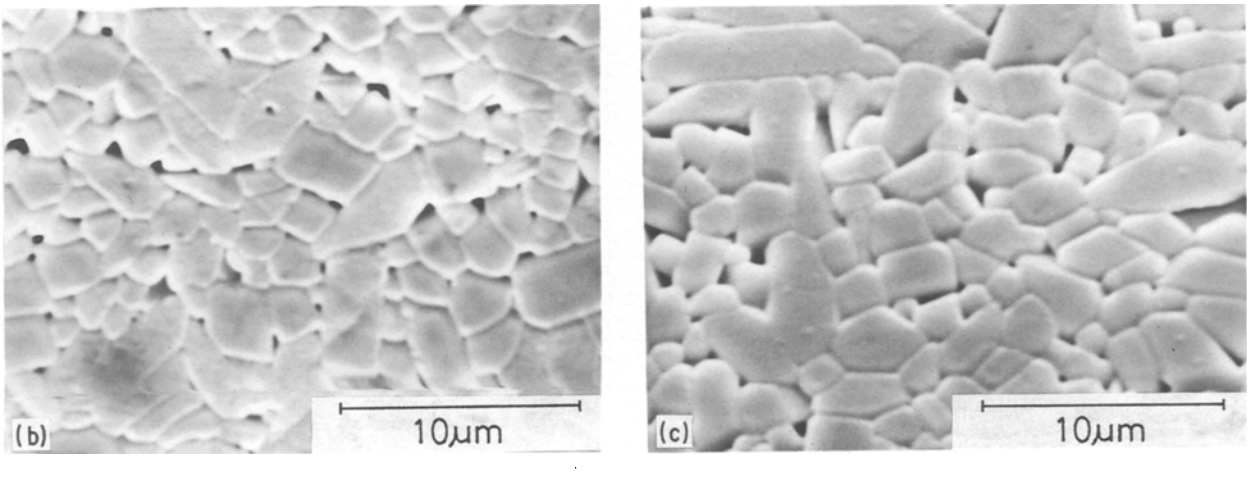


Figure 12 SEM microphotographs of mullite doped with (a) 0.5; (b) 0.30; (c) 0.75 wt % MgO sintered at 1700° C for 3 h.



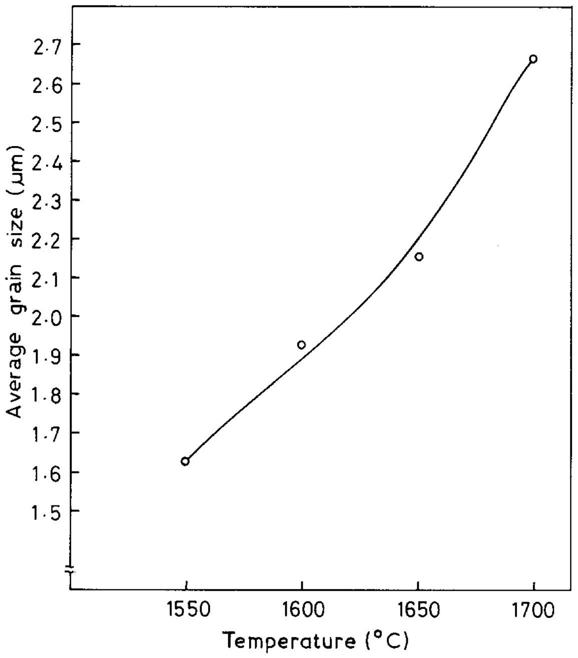


Figure 13 Influence of temperature on the average grain size of mullite containing 0.5 wt % MgO.

Figure 14 TEM microphotograph of mullite doped with 0.3 wt % MgO sintered at 1600° C for 3 h.

trations varying from 0.01 to 1.0 wt % were pressed into rectangular blocks and sintered. The sintering temperature was varied between 1640 and 1550° C, in decreasing order with increasing MgO concentration. The three-point bend strength was determined and was in the range of 300 MPa, irrespective of the MgO dopant concentration. The variation of flexural strength of mullite doped with 0.3 wt % MgO with temperatures up to 1400° C is given in Fig. 15. With the increase in temperature, the bend strength increases to 450 MPa at 1000° C and decreases to 300 MPa at 1300° C. On a further increase of temperature, the bend strength drops below 200 MPa at 1400° C. This is a clear indication of the effect of the glassy layer at the grain boundaries. The fracture toughness determined by the micro-indentation method also did not show any remarkable deviation with respect to MgO dopant concentration.

The coefficient of thermal expansion determined for compositions containing up to 0.75 wt % MgO was the same, and the value obtained was $\alpha_{20\text{-}400^\circ\mathrm{C}}$ – 4.43×10^{-6} °C. The dielectric constant measured at a frequency of 1 MHz was within 7.1 ± 0.2 for all compositions studied.

4. Conclusions

MgO-doped mullite gel powder prepared by the sol–gel method showed a decrease in mullitization temperature with increased MgO concentration. Addition of MgO in quantities over 0.3 wt % promotes the crystallite growth of mullite. The temperature required for sintering mullite to a relative density > 98% decreased with the increase of MgO dopant concentration. Pure mullite requires temperatures in the region of 1650° C to achieve a relative density of > 98%, whereas the addition of MgO in quantities over 0.3 wt % enhance the densification rate and could be sintered to a relative density > 98% at

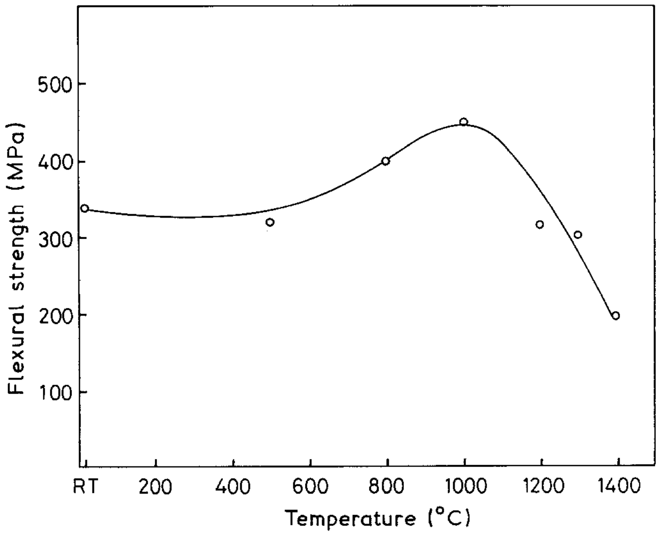


Figure 15 Variation of three-point bend strength of mullite doped with 0.30 wt % MgO with temperature.

temperatures low as 1550° C. The grain morphology observed was equiaxed, and with the increase in sintering temperature a part of MgO volatalizes with the exsolution of Al_2O_3 and SiO_2 from mullite grain leading to a glassy layer along the grain boundary. The morphology of the grains was changed at this stage to acicular or needle-like. The mechanical, thermal and electrical properties did not change with the MgO dopant concentration studied.

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