ELSEVIER

Journal of Materials Processing Technology 142 (2003) 275–281

Journal of
Materials
Processing
Technology

www.elsevier.com/locate/jmatprotec

Effect of MgO, Y_2O_3 and boehmite additives on the sintering behaviour of mullite formed from kaolinite-reactive alumina

V. Viswabaskaran [a,1], F.D. Gnanam [a,2], M. Balasubramanian [b,*]

[a] Centre for Ceramic Technology, Alagappa College of Technology, Anna University, Chennai 600025, India
[b] Department of Metallurgical Engineering, Composites Technology Centre & Department of Metallurgical Engineering,
Indian Institute of Technology, Chennai 600036, India

Received 24 June 2002; accepted 26 February 2003

Abstract

Reaction sintering of clay and reactive alumina is an innovative as well as cost effective method of mullite formation. In the present investigation, clay obtained from Neyveli (South India) and reactive alumina (mean particle size of 0.7 μm) were used as starting materials. To improve the densification of mullite, magnesia and yttria (1–5 wt.%) were used as sinter additives to the above materials. Boehmite was partly substituted for reactive alumina (1–7 wt.%). As per the stoichiometric composition the raw materials were mixed, uniaxially pressed and sintered at 1500, 1550 and 1600 °C for 3 h. Among the sintered samples, the samples sintered at 1600 °C exhibited better properties. The 3 wt.% MgO addition showed improved density up to 2.91 g cm^{-3} with the maximum strength of 125 MPa. Y_2O_3 addition favoured the development of equiaxed mullite, but did not help to increase the density and strength. The boehmite substitution (5 wt.%) yielded maximum density of 96% theoretical density (3.01 g cm^{-3}) and strength of 120 MPa. Microstructural studies showed that the addition of boehmite resulted in a blend of small to bigger crystals throughout the structure.

Keywords: Mullite; Clay; Meta-kaolinite; Reactive alumina; Boehmite

1. Introduction

Mullite, ideally $3Al_2O_3{\cdot}2SiO_2$, is a high melting crystalline alumino-silicate material which has long been used in heavy-duty refractories [1]. In the last decade, the need to produce high quality mullite for optical, dielectric and structural applications has lead to numerous studies on the synthesis and processing of mullite [2]. Both conventional and non-conventional methods have been successfully used to synthesis mullite, such as simple sintering of alumina and silica powders [3], sol–gel [4], co precipitation [5], hydrothermal [6], flash combustion [7] and chemical vapour deposition [8]. The production of high purity, high density mullite by the above methods are expensive [9]. On the other hand, starting with cheap raw materials like kaolinite, kaolinite–alumina and sillimanite minerals, it is possible to produce high purity mullite and the properties obtained through conventional ceramic processing and sintering is outstanding [10].

It is well known that kaolinite undergoes a series of reactions during the early stages of heating and finally forms mullite with the segregation of SiO_2 [11]. The reaction of kaolinite with alumina is of interest in the production of mullite by reaction sintering [12]. At temperatures below 1300 °C, the reaction between kaolinite and alumina is limited and at this stage, the primary mullite crystals are formed by the decomposition of meta-kaolinite. At temperatures above 1400 °C, secondary mullite formation takes place by the dissolution of alumina into transitory liquid silica phase, followed by the precipitation of mullite crystals [13]. The rate of secondary mullite formation is very slow till the eutectic liquid formation at 1587 °C and extremely fast at 1600 °C [12].

Mullite powder compacts have poor solid state sinterability because of the low interdiffusion rates of Si^{4+} and Al^{3+} within the mullite lattice [9]. MgO [14–16] and Y_2O_3 [7] have been reported as good sintering aids for the fused mullite. Boehmite [17] was a successful sintering aid for sol–gel mullite to sinter at a relatively lower temperature. The study reported in this paper, compared the effect of MgO, Y_2O_3

---

[*] Corresponding author. Tel.: +91-44-22578609/22578704;
fax: +91-44-22570039/22570545.
E-mail addresses: zeramist@yahoo.co.in (V. Viswabaskaran),
fdgnanam@yahoo.com (F.D. Gnanam),
mbala@iitm.ac.in (M. Balasubramanian).
[1] Tel.: +91-44-24422170.
[2] Tel.: +91-44-22431248; fax: +91-44-2352870.

0924-0136/$ – see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0924-0136(03)00577-6

and boehmite additives on kaolinite-reactive alumina mixture sintered at three different temperatures 1500, 1550 and 1600 °C. The X-ray diffraction and microstructural studies are carried out with different concentration of additives. The physical properties, such as open porosity, bulk density and bending strength are also performed and reported.

2. Experimental

Experiments were carried out on raw kaolinite from Neyveli (South India) with reactive alumina (Alcoa SG 9000, mean particle size 0.7 μm). As per the stoichiometric composition (72 wt.% of Al_2O_3), the above materials were carefully weighed. MgO ($MgCO_3$) or Y_2O_3 of concentrations varying from 1 to 5 wt.% was mixed with the above composition for making different batches. Boehmite (synthesised from aluminium isopropoxide [18]) was added as a substitute for the reactive alumina from 1 to 7 wt.%. The various batches were wet milled for half an hour in a planetary mill using alumina balls for thorough mixing. Finally, the slurries were dried at 100 °C for 72 h [13]. Rectangular bars (5 mm × 5 mm × 50 mm) were produced by uniaxial pressing of the 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 at 1500, 1550 and 1600 °C and soaked for 3 h before furnace cooling.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) experiments were carried out using NETZSCH STA 409PC with α-alumina as the reference material, at a heating rate of 5 °C min^{-1} in air. The powder samples of −200 ASTM mesh size were dried at 110 °C for 2 h before thermal analysis. The phases present in sintered samples were identified by X-ray diffraction (XRD) technique using Siemens D-500 powder diffractometer using Cu Kα radiation. For XRD analysis, the powders were prepared from the compacts heated at the same rate as that of DTA analysis. The bulk density of the samples was measured by Archimedes principle. Modulus of rupture (MOR) was determined on the polished surfaces of the rectangular samples sintered at different temperatures, using universal testing machine (Zwick 1445). All the physical tests were carried out on a minimum of 10 samples and the results were then averaged. The samples were polished and thermally etched for 1 h at a temperature 100 °C lower than the sintering temperature and subsequently examined under scanning electron microscope (SEM) using Cambridge Instruments-5526 scanning electron microscope.

3. Results and discussion

Table 1 shows the chemical composition in weight percentages of Neyveli clay and reactive alumina. The clay contains moderate amount of impurities and is the best available clay source in the state of Tamil Nadu, India [19] and has a mean particle size of 2.0 μm. Reactive alumina is pure and having narrow particle size distribution with mean particle size of 0.7 μm. DTA curves of clay and clay-reactive alumina are shown in Fig. 1. The two endothermic peaks at 110 and 550 °C are due to loss of absorbed and structural water, respectively. There is a prominent exothermic peak at around 980 °C and a much smaller exothermic peak in between 1200 and 1250 °C in the derivative curve (not visible in figure). This is due to the formation of 2:1 mullite and spinel from meta-kaolinite, followed by 3:2 mullite formation [13]. TGA results also confirm that the two endothermic peaks in DTA are due to the loss of absorbed and structural water removal from clay (Fig. 2).

Table 1
Chemical analysis of raw materials

Constituent	Neyveli clay (wt.%)	Reactive alumina (wt.%)
LOI	16.00	–
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	–

The XRD results of samples sintered at 1600 °C for 3 h are shown in Fig. 3. There is no evidence for the presence of cristobalite and α-alumina peaks in the samples having 1 wt.% MgO. This confirms that the reaction of clay and reactive alumina at 1600 °C for 3 h is sufficient for the formation of mullite. However, the samples with 2 and 3 wt.% MgO additions show the presence of

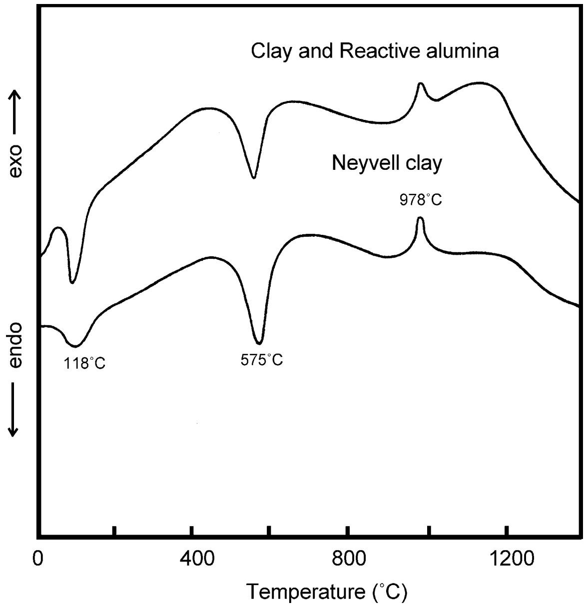

Fig. 1. Differential thermal analysis of clay and clay + reactive alumina mixtures.

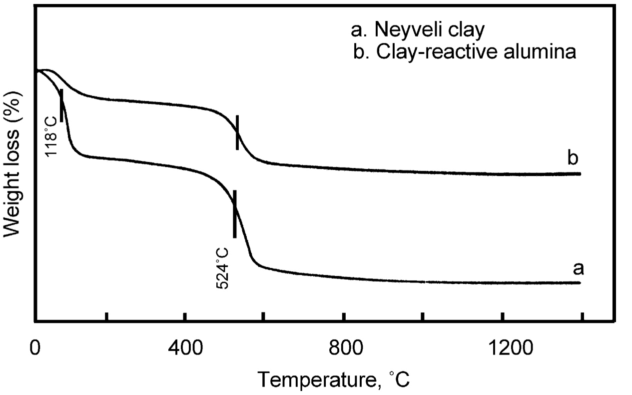

Fig. 2. Thermogravimetric analysis of clay and clay + reactive alumina mixtures.

secondary phases such as α-alumina and MgO–Al_2O_3 spinel. Many authors [7,14,15] 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 can be understood from the MgO–Al_2O_3–SiO_2 phase diagram [14] that MgO can produce a MgO–Al_2O_3 spinel at high temperatures. However, at temperatures above the peritetectic point (1578 °C for pure system), the equilibrium phases are mullite, α-Al_2O_3 and liquid. According to the phase diagram, the spinel phase does not exist above the peritetectic point. The MgO–Al_2O_3 spinel crystals are formed as a result of devitrification of the liquid phase during cooling. The mullite grains grow during devitrification, entrapping the spinel precipitates. This is the reason for the detection of small peaks of α-alumina and MgO–Al_2O_3 spinel for samples containing 3 wt.% MgO. The samples containing 1 wt.% MgO do not show any characteristic peaks of α-alumina and MgO–Al_2O_3 spinel. The XRD results of the samples sintered at 1550 °C for 3 h with MgO are similar to the samples sintered at 1600 °C. The substitution of reactive alumina with boehmite also results in the formation of complete mullite phase. On increasing the amount of boehmite, there is no marked change in the phase formation.

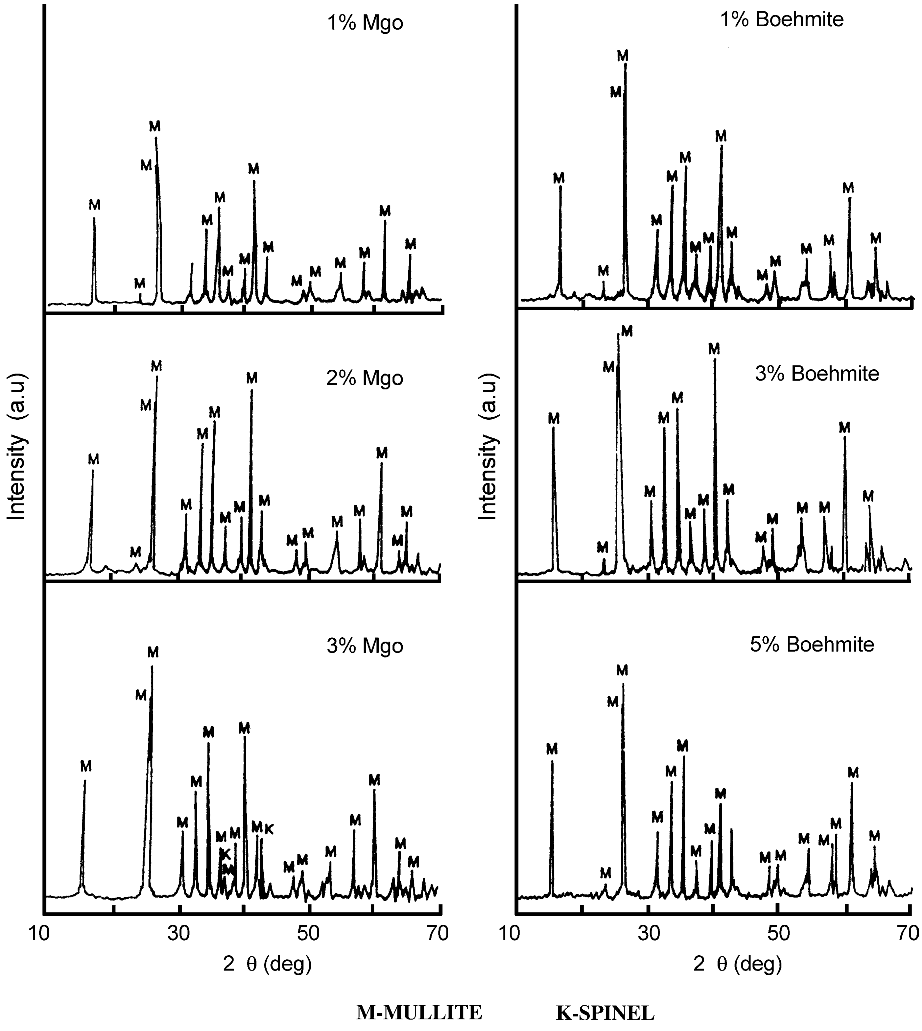

Fig. 3. XRD patterns of clay + reactive alumina with additives sintered at 1600 °C for 3 h.

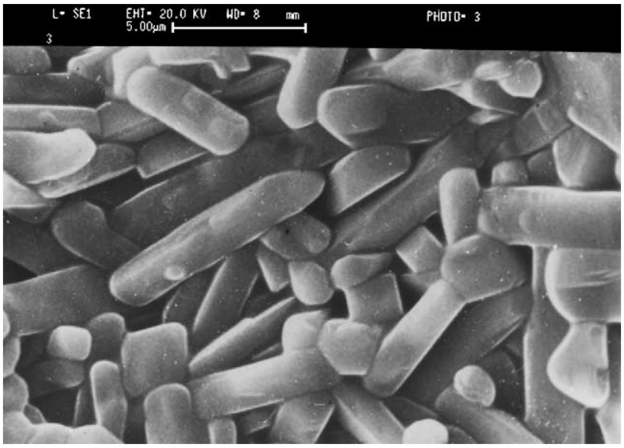

Fig. 4. Microstructures of clay + reactive alumina sintered at 1600 °C for 3 h.

The SEM microstructures of the samples sintered at 1600 °C for 3 h are shown in Figs. 4–7. The microstructural analysis of Neyveli clay-reactive alumina without additives (Fig. 4) shows that mullite crystals are bimodal [13], i.e. structure consists of larger elongated primary mullite grains and smaller more equiaxed secondary mullite grains. The primary mullite grains are tabular in shape, having rectangular faces with rounded ends. Several authors [12,13] have reported that during the heating of kaolinite–α-alumina mixtures, primary mullite is formed from the kaolinite above 980 °C, while secondary mullite is formed at higher temperatures by a solution–precipitation mechanism from the transitory liquid phase. For complete mullitisation of kaolinite–α-alumina mixture, the sintering temperature is around 1600 °C. The microstructure of clay-reactive alumina mixture with MgO is shown in Fig. 5. The increase in MgO content increases the size of the mullite grains. The enlarged mullite grains are predominantly observed for the sample containing 3 wt.% MgO compared to the sample containing 1 wt.% MgO. The accelerated grain growth reduces the pore volume and the grains are very closer in the case of sample containing 3 wt.% MgO. The primary mullite crystals are grown to 20 μm in length and 5–6 μm in width. Secondary mullite is also grown considerably in all the directions. Further increase in MgO content leads to visible bloating on the samples.

Fig. 6 shows the effect of yttria addition from 1 to 5 wt.%. The microstructure reveals that the yttria addition in the clay-reactive alumina mixture enhances the secondary mullite formation rather than the primary mullite formation. The increase in yttria increases the grain size of mullite. However, the increase in yttria is not causing any bloating or cracks in the samples.

Fig. 7 shows the microstructure of boehmite substituted clay-reactive alumina samples. The microstructure of the sample containing 1 wt.% boehmite shows the presence of more primary mullite than the secondary mullite. The mullite crystals are not equal in shape and size, and are widely distributed from 1 to 15 μm in length and 1 to 5 μm in width. As the amount of boehmite is increased the amount of secondary mullite also increases. There is no considerable grain growth by increasing the boehmite content. The distribution of primary and secondary mullites from kaolinite–boehmite mixtures are more homogeneous than with other additives, due to the mechanochemical reaction taking place in the presence of structural water from

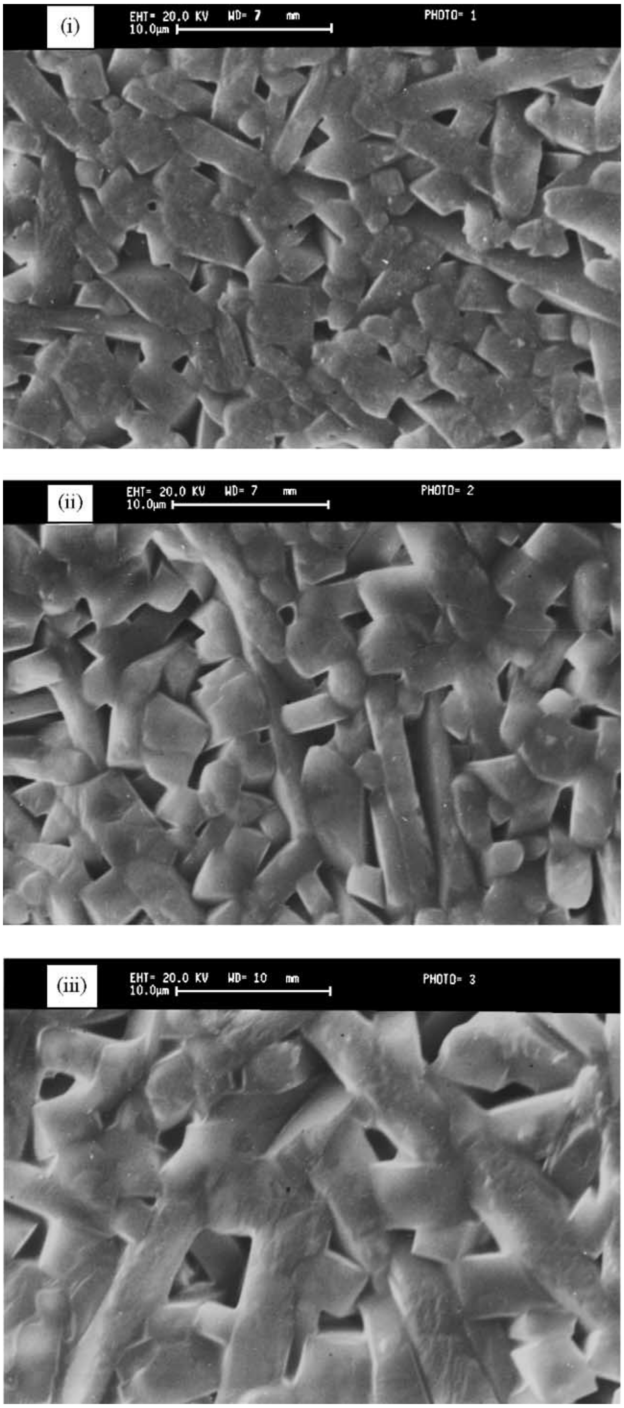

Fig. 5. Microstructures of clay + reactive alumina with MgO sintered at 1600 °C for 3 h: (i) 1 wt.% MgO; (ii) 2 wt.% MgO; (iii) 3 wt.% MgO.

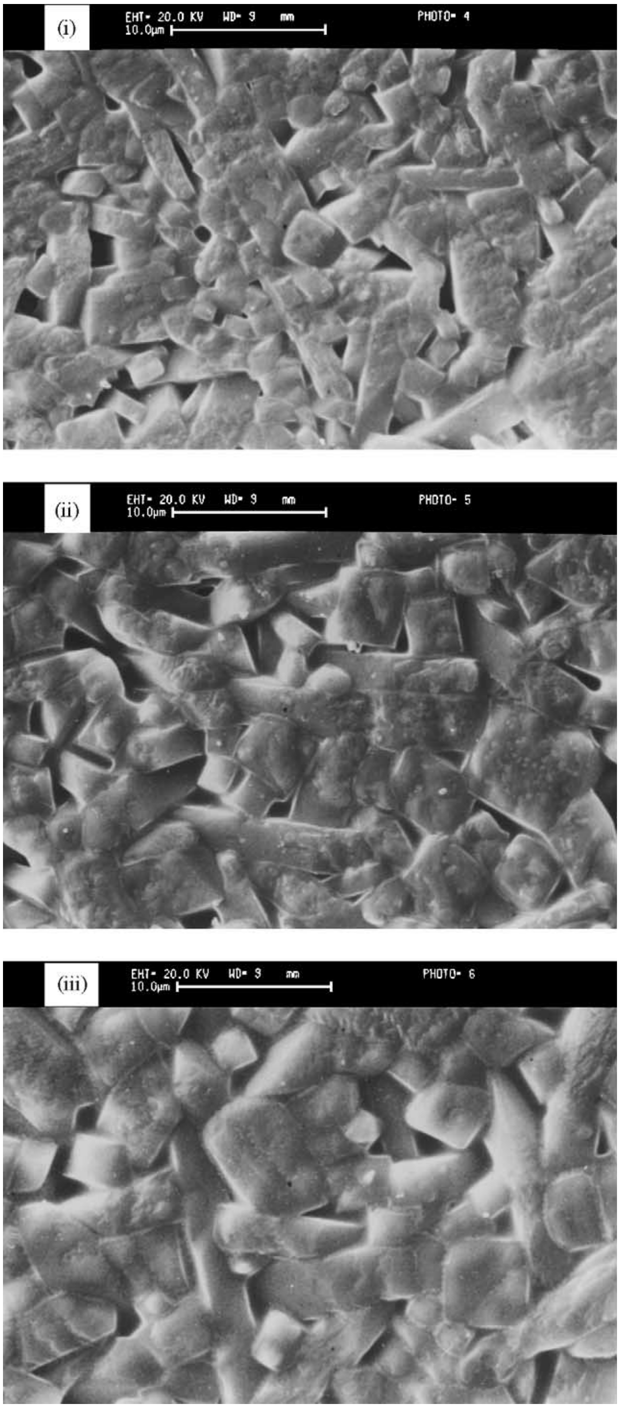

Fig. 6. Microstructures of clay + reactive alumina with yttria sintered at 1600 °C for 3 h: (i) 1 wt.% yttria; (ii) 3 wt.% yttria; (iii) 5 wt.% yttria.

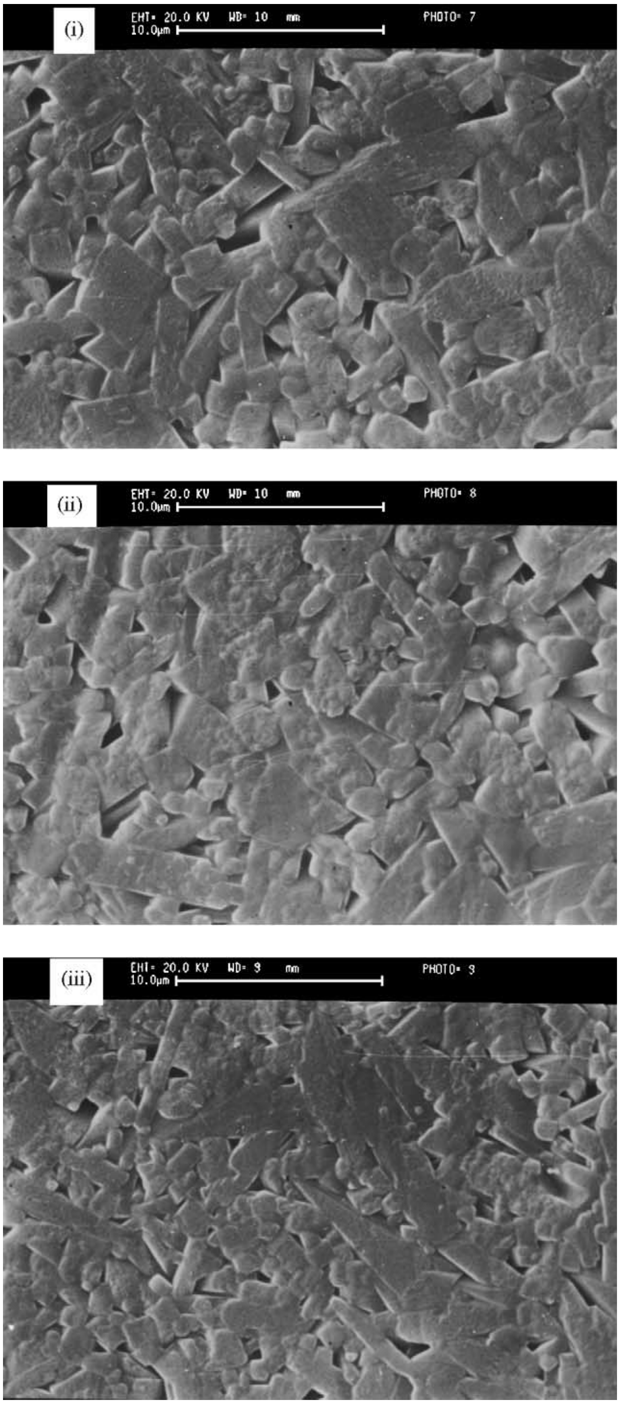

Fig. 7. Microstructures of clay + reactive alumina with boehmite sintered at 1600 °C for 3 h: (i) 1 wt.% boehmite; (ii) 3 wt.% boehmite; (iii) 5 wt.% boehmite.

the kaolinite and boehmite [20]. The secondary mullite is formed during thermal reaction by solution–precipitation mechanism. The 5 wt.% boehmite containing sample shows minimum pore area and large quantity of mullite crystals.

The physical properties of the samples sintered at 1500, 1550 and 1600 °C for 3 h are presented in Tables 2–4. The density of the samples sintered at 1500 and 1550 °C are comparatively lower than the samples sintered at 1600 °C. Correspondingly the flexural strength values are lower for the samples sintered at 1500 and 1550 °C.

The additions of MgO, Y_2O_3 and boehmite have considerable influence on the densification, when the samples are sintered at 1600 °C. The bulk density of samples sintered at 1600 °C for 3 h increases from 2.53 g cm^{-3} to a maximum value of 2.91 g cm^{-3} for 3 wt.% MgO addition. It is well

Table 2
Properties of sintered (1500 °C) clay-reactive alumina with additives

	Open porosity (%)	Bulk density (g cm^{-3})	MOR (MPa)
Without additives	8.03	2.53	41 (3)
1 wt.% MgO	1.36	2.74	48 (5)
2 wt.% MgO	0.77	2.78	52 (3)
3 wt.% MgO	0.68	2.80	73 (4)
1 wt.% Y_2O_3	1.57	2.76	39 (3)
3 wt.% Y_2O_3	1.28	2.77	47 (3)
5 wt.% Y_2O_3	1.23	2.77	54 (4)
1 wt.% boehmite	7.62	2.68	39 (3)
3 wt.% boehmite	4.97	2.65	41 (4)
5 wt.% boehmite	4.53	2.65	46 (3)

Table 3
Properties of sintered (1550 °C) clay-reactive alumina with additives

	Open porosity (%)	Bulk density (g cm^{-3})	MOR (MPa)
Without additives	5.25	2.69	47 (3)
1 wt.% MgO	0	2.81	83 (4)
2 wt.% MgO	0	2.82	89 (5)
3 wt.% MgO	0	2.82	94 (7)
1 wt.% Y_2O_3	1.34	2.78	44 (3)
3 wt.% Y_2O_3	1.15	2.80	56 (3)
5 wt.% Y_2O_3	0.69	2.82	58 (4)
1 wt.% boehmite	1.35	2.75	83 (5)
3 wt.% boehmite	1.02	2.79	88 (6)
5 wt.% boehmite	0.70	2.85	97 (5)

known that MgO accelerates the densification process in alumina by modifying the lattice diffusion [9]. Similarly, MgO enhances the densification of mullite. Diffusion of MgO and SiO_2 from mullite grains favours the formation of a liquid phase along the grain boundary and thereby densification takes place [14–16]. Thus, the addition of MgO accelerates the mullite grain growth and reduces the pore volume. This is the reason for the improved density and strength. However, an excess amount of MgO does not help to improve the properties rather increases the formation of low melting silicate that causes bloating. The addition of 3 wt.% MgO results in a maximum bending strength of 126 MPa. Further increase in MgO leads to bloating and that lowers the strength. The bending strength values are noticeably higher for the samples sintered at 1600 °C than the samples sintered at lower temperatures.

Table 4
Properties of sintered (1600 °C) clay-reactive alumina with additives

	Open porosity (%)	Bulk density (g cm^{-3})	MOR (MPa)
Without additives	4.35	2.71	82 (3)
1 wt.% MgO	0	2.82	99 (5)
2 wt.% MgO	0	2.84	115 (7)
3 wt.% MgO	0	2.91	126 (5)
4 wt.% MgO	0	2.83	Bloat
5 wt.% MgO	0	2.53	Bloat
1 wt.% Y_2O_3	1.2	2.78	84 (4)
3 wt.% Y_2O_3	0	2.83	96 (6)
5 wt.% Y_2O_3	0	2.83	95 (5)
1 wt.% boehmite	0	2.86	95 (4)
3 wt.% boehmite	0	2.92	106 (7)
5 wt.% boehmite	0	3.01	120 (5)
6 wt.% boehmite	0	2.91	Cracks
7 wt.% boehmite	0	2.83	Cracks

The addition of yttria in mullite aids the formation of a liquid phase at low temperature and promotes densification [7]. The Y_2O_3 addition shows moderate improvement in density and strength. The 1 wt.% Y_2O_3 increases the density from 2.71 to 2.78 g cm^{-3} and 5 wt.% Y_2O_3 increases the density to 2.83 g cm^{-3} after sintering at 1600 °C for 3 h. Similarly the strength increases from 82 to 96 MPa.

The boehmite substitution to reactive alumina leads to maximum bulk density (3.01 g cm^{-3}) compared to all other additives. This value equals to 96% theoretical density (3.16 g cm^{-3}, JCPDS no. 06-0258). The bending strength also increase from 82 to 120 MPa with increasing boehmite substitution. Further increase in the amount of boehmite leads to the formation of visible cracks and results in lower density and strength. The formation of cracks is due to higher loss of structural water with increasing amount of boehmite (boehmite contains ≈41% structural water).

The maximum strength of the samples with Y_2O_3 are comparatively lower than the maximum strength of the samples with MgO or boehmite. The presence of equiaxed secondary mullite throughout the system is the reason for the lower density and strength with Y_2O_3. Though the density of samples with 5 wt.% boehmite is the highest, the strength is not correspondingly the highest. This may be due to the wide size distribution of mullite grains and the presence of more secondary mullite.

4. Conclusion

The results of the present study indicate that the addition of MgO increases the grain growth and thereby increase the density to maximum value. The physical properties are good for 3 wt.% MgO and 5 wt.% substitution of boehmite samples sintered at 1600 °C. MgO enhances the liquid phase sintering and a density value of 2.91 g cm^{-3} is obtained for the 3 wt.% MgO addition. The amount of MgO beyond 3 wt.% induces bloating and thereby decreases the density. The maximum density achieved is 3.01 g cm^{-3} for 5 wt.% substitution of boehmite in place of reactive alumina. The maximum strength value is restricted to 120 MPa and this is lower than the value obtained (126 MPa) for 3 wt.% MgO added samples. The boehmite addition in the mixture increases the size distribution of mullite grains, but does not increase the over all grain growth. The boehmite increases the secondary mullite formation by solution–precipitation mechanism. The addition of boehmite above 5 wt.% as substitution for reactive alumina causes cracks due to high structural water loss while sintering. Though the addition of yttria enhances the liquid phase formation and equiaxed secondary mullite formation, it does not improve the density and strength.

References

[1] Y.M. Al-Jarsha, H.G. Emblem, K. Jones, A.M.D. Rahman, F.J. Davies, R. Wakefield, G.K. Sargent, Preparation, characterisation and uses of mullite grain, J. Mater. Sci. 25 (1990) 2873–2880.

[2] H. Schneider, K. Okada, J. Pask, in: K. Okada (Ed.), Mullite and Mullite Ceramics, Wiley, Chichester, 1994, pp. 4–246.

[3] M.D. Sacks, H. Lee, J.A. Pask, A review of powder preparation methods and densification procedures for fabricating high density mullite, in: S. Somiya, R.F. Davis, J.A. Pask (Eds.), Ceramic Transaction: Mullite and Mullite Composites, vol. 6, American Ceramic Society, Westerville, OH, 1990, pp. 167–208.

[4] D. Amutharani, F.D. Gnanam, Low temperature pressureless sintering of sol–gel derived mullite, Mater. Sci. Eng. A 264 (1999) 254–261.

[5] S.P. Chaudhuri, S.K. Partra, Preparation and characterisation of transition metal ion doped mullite, Trans. Br. Ceram. Soc. 96 (1997) 105–111.

[6] S. Somiya, M. Yoshimura, M. Suzuki, T. Yanaguchi, Mullite powder from hydrothermal processing, in: S. Somiya, R.F. Davis, J.A. Pask (Eds.), Ceramic Transaction: Mullite and Mullite Matrix Composites, vol. 6, American Ceramic Society, Westerville, OH, 1990, pp. 287–317.

[7] R. Gopi Chandran, B.K. Chandrashekar, C. Ganguly, K.C. Patil, Sintering and microstructural investigations on combustion processed mullite, J. Eur. Ceram. Soc. 16 (1996) 843–849.

[8] Y. Hirata, I.A. Aksay, S. Hori, H. Kaji, Processing of mullite powders processed by CVD, in: S. Somiya, R.F. Davis, J.A. Pask (Eds.), Ceramic Transaction: Mullite and Mullite Matrix Composites, vol. 6, American Ceramic Society, Westerville, OH, 1990, pp. 287–317.

[9] W.E. Lee, W.M. Rainforth, Ceramic Microstructures: Property Control by Processing, Chapman & Hall, London, 1994, pp. 299–311.

[10] M.A. Sainz, F.J. Serrano, J. Bastida, A. Caballero, Microstructural evolution and growth of crystallite size of mullite during thermal transformation of kyanite, J. Eur. Ceram. Soc. 17 (1997) 1277–1284.

[11] A.K. Chakraborthy, D.K. Ghosh, Reexamination of the kaolinite-to-mullite reaction series, J. Am. Ceram. Soc. 61 (1978) 170–173.

[12] K.C. Liu, G. Thomas, Time–temperature–transformation curves for kaolinite–α-alumina, J. Am. Ceram. Soc. 77 (1994) 545–552.

[13] H.R. Rezaie, W.M. Rainforth, W.E. Lee, Mullite evolution in ceramics derived from kaolinite, kaolinite with added α-alumina, and sol–gel precursors, Trans. Br. Ceram. Soc. 96 (1997) 181–187.

[14] L. Montanaro, C. Esnouf, C. Perrot, G. Thollet, G. Fantozzi, A. Negro, Sintering of industrial mullites in the presence of magnesia as a sintering aid, J. Am. Ceram. Soc. 83 (2000) 189–196.

[15] L. Montanaro, J.M. Tulliani, C. Perrot, A. Negro, Sintering of industrial mullites, J. Eur. Ceram. Soc. 17 (1997) 1715–1723.

[16] M.G.M.U. Ismail, H. Tsunatori, S. Nakai, Preparation of MgO-doped mullite by sol–gel method, powder characteristics and sintering, J. Mater. Sci. 25 (1990) 2619–2625.

[17] D. Amutharani, Ph.D. Thesis, Anna University, Chennai, India, 1998, pp. 105–120.

[18] M. Sathyakumar, Ph.D. Thesis, Anna University, Chennai, India, 2000, pp. 25–36.

[19] V. Viswabaskaran, M. Balasubramanian, F.D. Gnanam, Characterisation of aluminus clays from Tamil Nadu, Trans. Ind. Ceram. Soc. 61 (2002) 176–180.

[20] J. Temuujin, K.J.D. MacKenzie, M. Schmucker, H. Schneider, J. McManus, S. Wimperies, Phase evolution in mechanically treated mixtures of kaolinite and alumina hydrates (gibbsite and boehmite), J. Eur. Ceram. Soc. 20 (2000) 413–421.