

## Mullitisation behaviour of south Indian clays

V. Viswabaskaran<sup>a</sup>, F.D. Gnanam<sup>a</sup>, M. Balasubramanian<sup>b,\*</sup>

<sup>a</sup>Centre for Ceramic Technology, Alagappa College of Technology, Anna University, Chennai 600 025, India

<sup>b</sup>Composite Technology Centre and Department of Metallurgical Engineering, Indian Institute of Technology, Chennai 600 036, India

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### Abstract

The sintered mullite is produced commercially, using clay and alumina as the source materials. South India has an abundant quantity of high aluminous clay. The present article reports the results of the mullitisation behavior of three south Indian clays (Neyveli, Panruti and Udayarpalayam clays) and three different alumina sources, (reactive alumina, gibbsite and boehmite) to produce stoichiometric mullite. The raw materials as per the stoichiometric composition were weighed and wet milled in a planetary ball mill. The dried and powdered materials were passed through 75  $\mu\text{m}$  sieve, then uniaxially pressed at 50 kN to make bars, and finally the specimens were sintered at 1600 °C for 3 h under normal atmospheric condition. By reaction-sintering the clay-alumina mixture reacts to form mullite. Physical characterization such as bulk density and water absorption and the mechanical properties, like flexural strength of sintered specimens were also carried out. The Neyveli-reactive alumina mixture showed high density (2.71 g  $\text{cm}^{-3}$ ) and high strength (82 MPa). The impure Udayarpalayam clay–reactive alumina mixture shows high strength (87 MPa), but low density (2.65 g  $\text{cm}^{-3}$ ). Microstructural studies on sintered and polished samples and X-ray diffraction studies on sintered specimens are carried out to estimate the mullitisation behavior of individual clays. Among the three clays and the three alumina sources, Neyveli clay and reactive alumina mixture gave the maximum mullitisation. The specimens with boehmite exhibited poor mechanical properties as well as poor physical properties. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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### 1. 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, high thermal shock resistance and remarkable creep resistance [1]. Mullite has been synthesized in many ways, like simple sintering of alumina and silica powders [2], sol-gel [3], co-precipitation [4], hydrothermal [5] and chemical vapor deposition [6] processes. Even though the above processes yield chemically pure mullite, the processing technology and high cost of starting materials make the mullite costly and are consequently not appropriate for large scale production [7]. The production of high purity mullite requires pure starting materials and atomic scale

of mixing [8]. Due to the above reasons, clay still remains as the ever-cheaper alternative source to make mullite with addition of alumina. When aluminosilicate minerals are heated above 1400 °C, they react to form mullite and silica. A number of natural and synthetic materials have been utilized to produce alumina–mullite composites. In principle, alumina and silica mixed oxide powders, aluminosilicate based clays and minerals and hydrolysis of metal alkoxides have the potential to produce mullite upon heating.

In the kaolinite–alumina system, kaolinite is first dehydrated to meta-kaolinite in the temperature range of 500–600 °C. It has been reported that below 1300 °C alumina was largely inert and the dominant reactions were the kaolinite reaction series to form primary mullite, amorphous silica, and cristobalite [9]. At temperatures higher than 1400 °C, secondary mullite formation takes place from the transitory liquid phase, followed by precipitation of mullite crystals. The rate of the secondary mullite formation was very slow at 1555 °C and extremely fast at 1600 °C due to the strong effect of the eutectic liquid formation at 1595 °C [9–10]. In the

\* Corresponding author: Tel.: +91-44-4458609/4459609; fax: +91-44-2301039/2352545.

E-mail addresses: vvb@annauniv.edu (V. Viswabaskaran), mbala@iitm.ac.in (M. Balasubramanian), fdgnanam@yahoo.com (F.D. Gnanam).

present study, three beneficiated local clays were mixed with three different alumina sources (reactive alumina, gibbsite and bohemite) and subsequently reaction-sintered to produce mullite. Microstructural studies on the samples sintered at 1600 °C have been carried out. To understand the mullite formation, thermal and physical characterisation were also performed.

## 2. Experimental procedure

Three different clays from the southern part of India namely Neyveli, Panruti and Udayarpalayam [11] were examined with addition of reactive alumina (Alcoa SG9000), gibbsite (Indal) and bohemite (synthesized from aluminium isopropoxide). Particle size distribution analyses were carried out for the starting raw materials using Shimadzu laser particle size analyzer (model SALD 1100). Powders were subjected to differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) using NETZSCH STA409PC with  $\alpha$ -alumina as the reference material at a heating rate of 5 °C min<sup>-1</sup> in air. The powder samples of -200 ASTM mesh size were dried at 110 °C for 2 h before thermal analysis.

The beneficiated clays [11] were mixed with an alumina source to give a total of 72 wt.% alumina for stoichiometric mullite [12]. The aluminas and the clays were mixed with water and wet milled for half an hour in a planetary mill using alumina milling media. After complete homogenization, the slurries were dried at

100 °C for 72 h [13]. The dried powder was again dry milled to break the soft agglomerate and was passed through a 75  $\mu$ m sieve. Bars of dimensions 50×5×5 mm<sup>3</sup> were made by uniaxial pressing in a steel die at 50 kN and were fired in an electric furnace at a heating rate of 5 °C min<sup>-1</sup> in air to 1600 °C and soaked for 3 h before furnace cooling. Simultaneously bars of pure clay were also prepared and sintered along with the above specimens. The samples made of pure clays were used to study the characteristic of cristobalite formation in the absence of alumina.

The minerals present in clays were identified by X-ray diffraction technique (XRD) using Siemens D-500 powder diffractometer, with CuK $\alpha$  radiation. For XRD analyses, the compacts were heated at the same rate as that of the DTA analyses, and powdered. The bulk

Table 1  
Chemical analysis of raw materials

Elements	Panruti clay (%)	Neyveli clay (%)	Udayarpalayam clay (%)	$\alpha$ -Alumina (%)	Gibbsite (%)
LOI	13.42	16.00	13.70	–	32.77
SiO <sub>2</sub>	49.06	43.26	52.09	0.01	0.18
Al <sub>2</sub> O <sub>3</sub>	33.07	36.11	29.92	99.85	64.35
Fe <sub>2</sub> O <sub>3</sub>	2.22	1.06	1.83	0.02	0.23
TiO <sub>2</sub>	1.20	1.59	0.78	–	–
CaO	0.51	0.37	1.03	0.01	2.22
MgO	0.23	1.40	0.48	–	0.02
Na <sub>2</sub> O	0.19	0.11	0.16	0.08	0.25
K <sub>2</sub> O	0.11	0.10	–	–	–

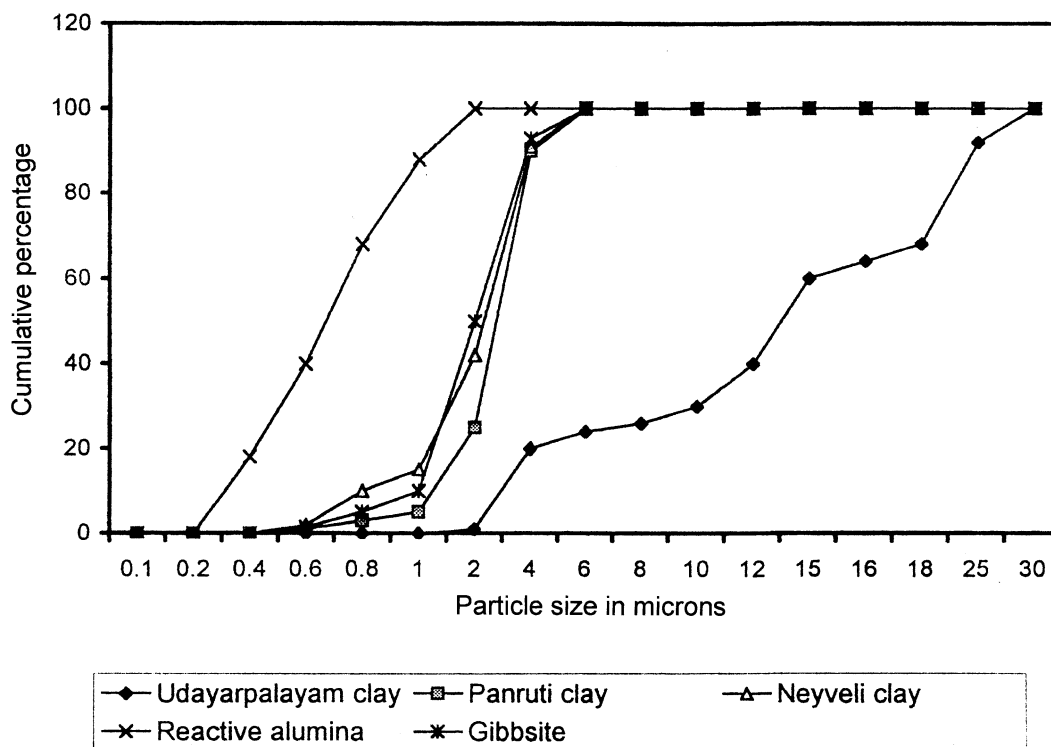


Fig. 1. Particle size distribution of raw materials.

density measurements of the pellets were carried out using the Archimedes principle. The modulus of rupture (MOR) was determined on rectangular samples fired at 1600 °C/3h using a universal testing machine (Zwick 1445). All the physical tests were carried out for a minimum three samples and the results then averaged. The samples were polished and thermally etched for 1 hr at 100 °C lower than the sintering temperature and subsequently examined under Cambridge Instruments-5526 scanning electron microscope (SEM).

### 3. Results and discussion

The chemical composition of the starting materials used in the investigation is presented in Table 1. It clearly shows that the percentage of impurity is higher in Panruti and Udayarpalayam clays. Among the three clays, Neyveli clay has moderate impurities and high loss on ignition due to the presence of carbonaceous impurities. Among the alumina sources, gibbsite has the highest impurities. The particle size distributions of the

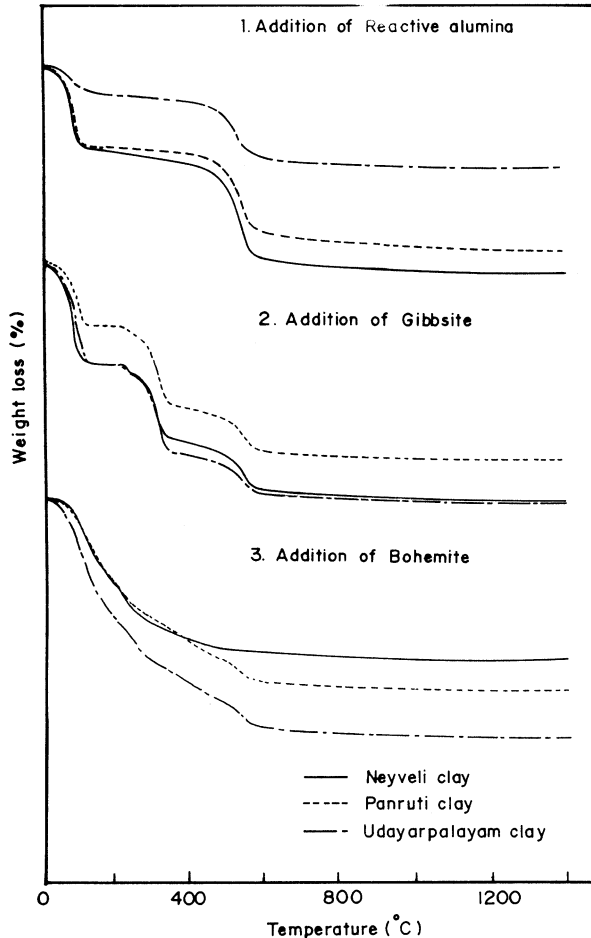


Fig. 2. Thermogravimetric analysis of clay + alumina mixtures.

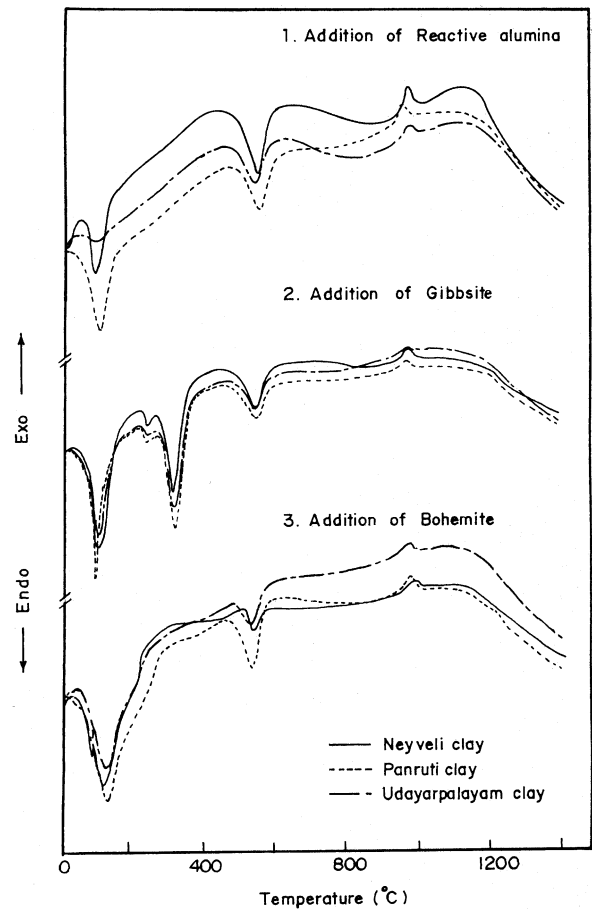


Fig. 3. Differential thermal analysis of clay + alumina mixtures.

Table 2  
Physical properties of clays with alumina additives (1600 °C/3h)

	Porosity (%)	Bulk density (g cm <sup>3</sup> )	MOR (MPa)
Neyveli clay + alumina	4.35	2.71	82.05
Neyveli clay + gibbsite	3.23	2.63	80.80
Neyveli clay + bohemite	14.88	2.40	21.90
Panruti clay + alumina	3.29	2.60	74.25
Panruti clay + gibbsite	0.70	2.64	78.75
Panruti clay + bohemite	21.03	2.16	20.01
Udayarpalayam clay + alumina	2.93	2.65	86.45
Udayarpalayam clay + gibbsite	0.00	2.54	80.60
Udayarpalayam clay + bohemite	18.72	2.22	26.80

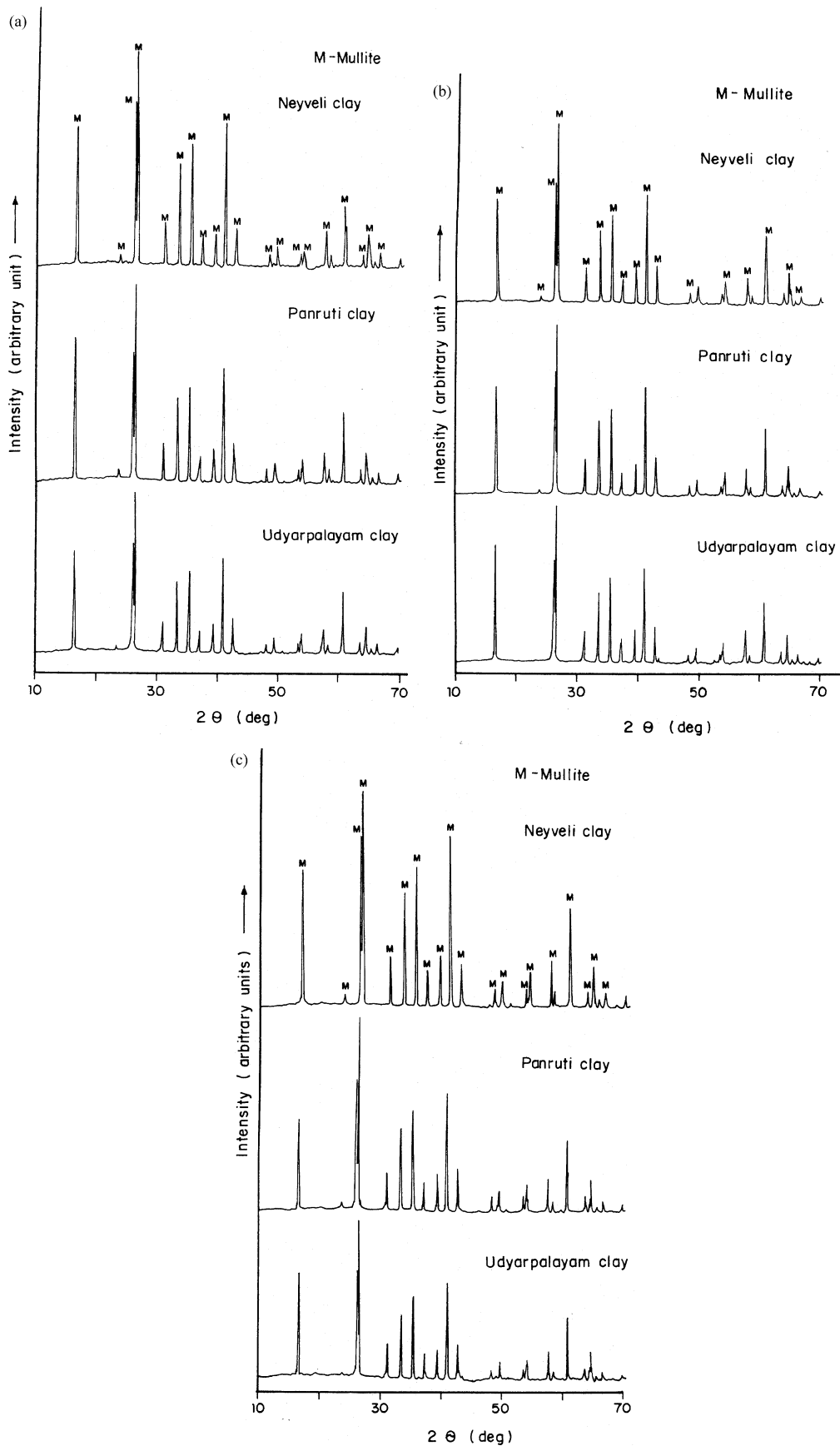


Fig. 4. XRD patterns of (a) clay-alumina fired at 1600 °C for 3 h; (b) gibbsite fired at 1600 °C for 3 h; (c) boehmite fired at 1600 °C for 3 h.

raw materials are given in Fig. 1. The mean particle size ( $d_{50}$ ) of the reactive alumina is 0.7  $\mu\text{m}$  and that of gibbsite is 2.0  $\mu\text{m}$ . The particle size and distribution of Neyveli and Panruti clays are very small and narrow, while Udayarpalayam clay contains coarse and wide particle size distribution.

The results of thermogravimetric analyses of samples are given Fig. 2. The weight loss occurred in clay-reactive alumina mixture at two temperature levels. The first one is around 110  $^{\circ}\text{C}$  and is due to adsorbed water and the second one is around 550  $^{\circ}\text{C}$  due to evaporation of structural water in clays.

In the clay gibbsite mixture, the weight loss occurred in four stages; at 110, 250, 325 and 550  $^{\circ}\text{C}$ . The weight losses at 110 and 550  $^{\circ}\text{C}$  are due to loss of adsorbed and structural water in clay respectively. The weight losses around 250 $^{\circ}$  and 325  $^{\circ}\text{C}$  are due to losses of structural water from gibbsite [16].

The DTA results (Fig. 3) of the clay and alumina mixture revealed an endothermic peak at about 110  $^{\circ}\text{C}$  originated from vaporization of adsorbed water. The broad second endothermic effect at 550  $^{\circ}\text{C}$  is due to loss of structural water with the formation of dehydroxylated kaolinite, i.e. meta-kaolin. The prominent exothermic peak at 980  $^{\circ}\text{C}$  corresponds to the formation of 2:1 mullite and spinel from meta-kaolin. A much smaller exothermic peak was found between 1200 to 1250  $^{\circ}\text{C}$  in the derivative curve (not visible in figure) associated with 3:2 mullite formation [13]. The DTA results of clay–gibbsite samples revealed two additional endothermic peaks with the above results of clay and alumina samples. The two endothermic peaks at 250 and 325  $^{\circ}\text{C}$  are due to vaporisation of structural water in gibbsite.

The physical properties of samples are given in Table 2. The maximum density was achieved at 1600  $^{\circ}\text{C}$  after 3 h (2.71  $\text{g cm}^{-3}$ ) for Neyveli clay with reactive alumina sample. For this sample the MOR value is also high (82 MPa). Poorer density and strength are noted for all boehmite containing samples due to visible minor cracks on the surfaces. The impurities present in raw materials are improving the strength but not density. The Udayarpalayam clay–alumina mixture shows maximum strength (86 MPa) and low density (2.65  $\text{g cm}^{-3}$ ) with 2.93% porosity. The same clay with gibbsite shows the strength of about 80 MPa with 2.54  $\text{g cm}^{-3}$  density and zero porosity. This shows that the impurities increase the glassy melt and remove the open pores and the result is an increase in strength.

XRD patterns for powders of different clay with alumina sources are shown in Figs. 4 (a)–(c). They clearly indicate that there is no cristobalite and  $\alpha$ -alumina peak in any sample. This confirms that the reaction of clay and alumina sources at 1600  $^{\circ}\text{C}$  for 3 h is sufficient to convert them into mullite. Though the conversion is

good in all samples, the peak intensity for mullite is varying with alumina and clay sources. Among the samples, the peak intensity is maximum for Neyveli clay and minimum for Udayarpalayam clay. XRD patterns for powders of different clays fired at 1600  $^{\circ}\text{C}$  are shown in Fig. 5. There is no crystalline silica phase (cristobalite phase), but there is enough evidence to confirm that silica is present in glassy form.

From the microstructural analysis (Fig. 6(a)–(c)) of the specimens, it is possible to observe that mullite crystals are bimodal in size [14]. The sizes of the primary mullite crystals are larger than the secondary mullite crystals. The size and shape of mullite crystals are different in different specimens. The micrograph for Neyveli clay with reactive alumina mixture shows that the mullite grains are tabular in shape, having rectangular faces with rounded ends (Fig. 6a). The Panruti and alumina mixture yields the irregular shape, whereas the Udayarpalayam with alumina mixture does not show perfect needle shape and all the crystals are surrounded by glassy matrix.

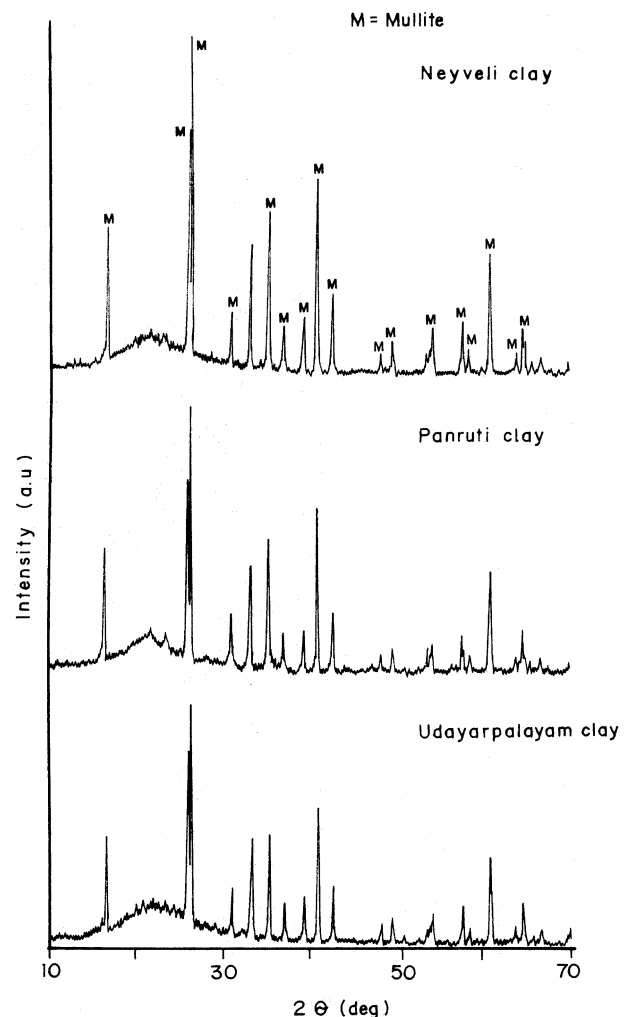


Fig. 5. XRD patterns of clays fired at 1600  $^{\circ}\text{C}$  for 3 h.

The micrographs of clay–gibbsite are also not showing the presence of characteristic mullite crystals. In the Neyveli clay, the crystals are with imperfect ends, whereas Panruti clay shows larger pores along with mullite crystals. The Udayarpalayam clay does not show any perfect crystals. The microstructure of clay–boehmite mixture gives different micrographs. Boehmite samples yield lengthy needle shaped crystals for all the clay samples. The size of the primary mullite grains in Neyveli and Panruti clay base mixture are higher than 10  $\mu\text{m}$  and width is 1–2  $\mu\text{m}$ .

The microstructure of clay samples fired at 1600  $^{\circ}\text{C}$  is shown Fig. 7. The Neyveli clay shows that the perfect primary mullite crystals are having sharp edges. The number of secondary mullite crystals observed is minimum. In Panruti clay, the secondary mullite crystals are seen with well crystallized sharp edged needles. In Neyveli and Panruti clays the mullite needles show high aspect ratio. The Udayarpalayam clay micrograph clearly shows that both the primary and secondary mullite are having round edges due to the impurities.

The poor solid state sinterability of mullite powder is explained elsewhere [1]. The very low interdiffusion rates of  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  with the mullite lattice mean that the kinetics of forming mullite by reaction depend strongly on the starting materials and intensive mixing [8]. However the impurities present in the clay and gibbsite form liquid phase to assist mullitisation and densification [15]. The chemical analysis report confirms that the clays (except Neyveli clay) contain high impurities that strongly affect the mullitisation. The TGA and DTA results resemble the result of pure kaolin and in addition have endothermic peaks due to structural water loss in gibbsite and boehmite. The exothermic reaction at high temperature (1200–1250  $^{\circ}\text{C}$ ) is due to 3:2 mullite formation from meta-kaolin [13]. There are no evident exothermic peaks due to the reaction of clay and alumina for the entire system up to 1400  $^{\circ}\text{C}$ . Maximum density and strength were achieved for Neyveli-alumina mixture due to low impurity and fine grain size. The impurities present in gibbsite and also the larger particle size are responsible for the poor mullitisation of two clays.

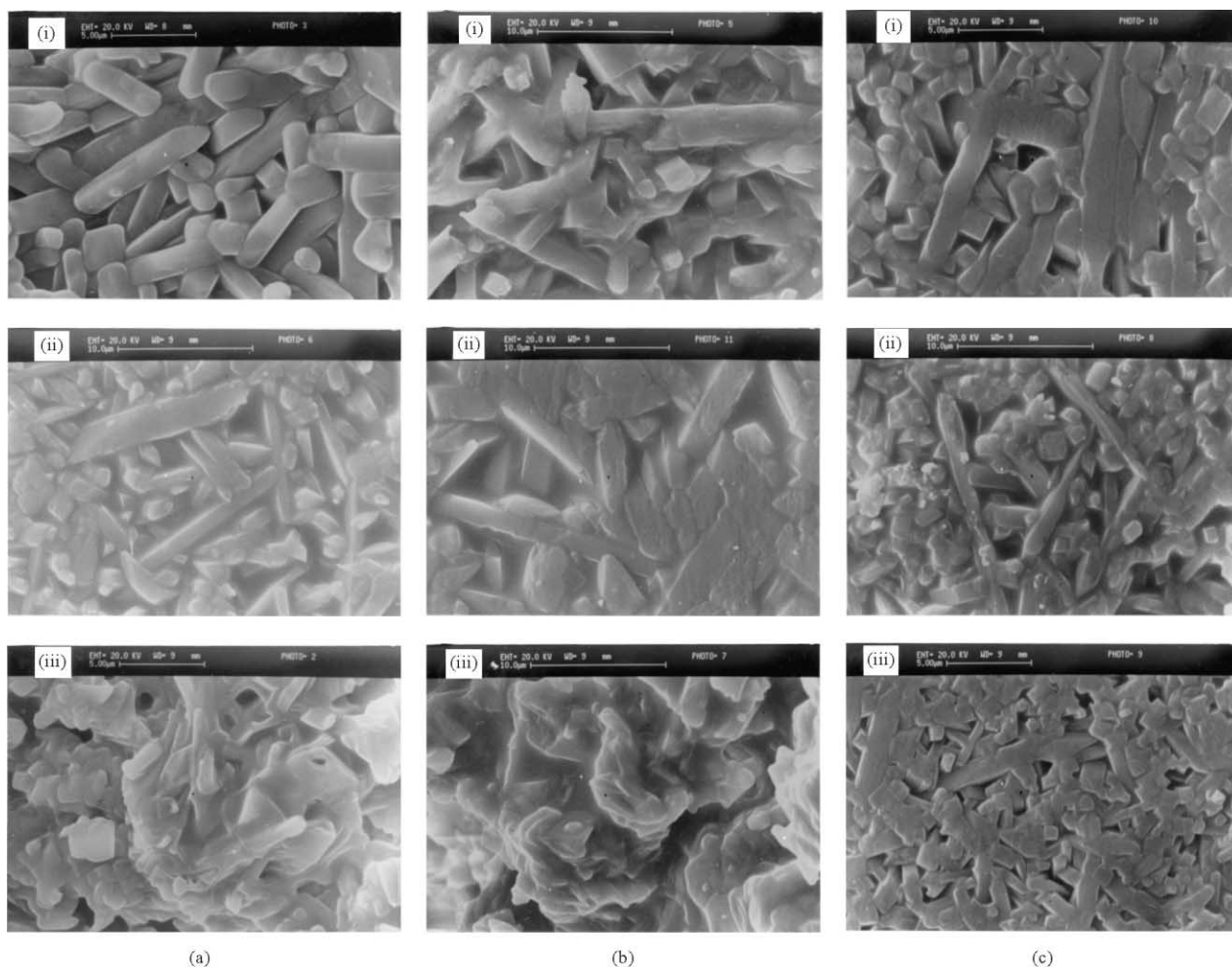


Fig. 6. Microstructures of clay–alumina fired at 1600  $^{\circ}\text{C}$  for 3 h. (i) Neyveli clay, (ii) Panruti clay and (iii) Udayarpalayam Clay; (b) Clay–gibbsite fired at 1600  $^{\circ}\text{C}$  for 3 h. (i). Neyveli clay, (ii). Panruti clay and (iii). Udayarpalayam Clay; c Microstructures of clay – boehmite fired at 1600  $^{\circ}\text{C}$  for 3 h. (i) Neyveli clay, (ii) Panruti clay and (iii) Udayarpalayam Clay.

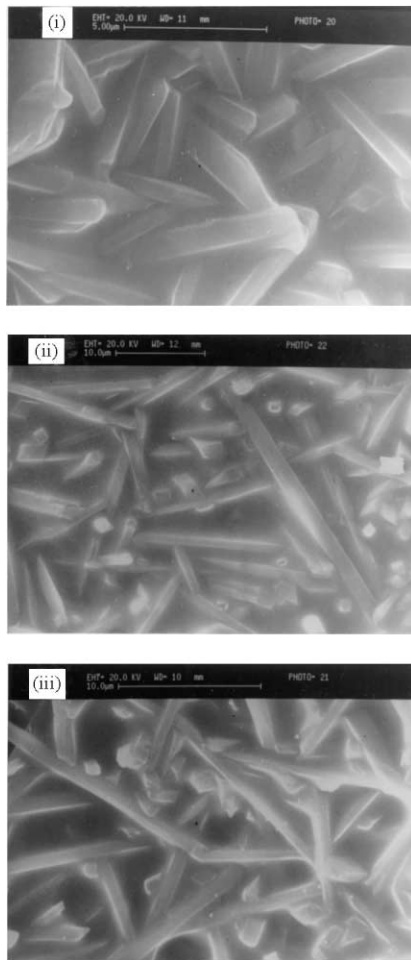


Fig. 7. Microstructures of clays fired at 1600 °C for 3 h (i) Neyveli clay, (ii) Panruti clay and (iii) Udayarpalayam clay.

In the boehmite samples, cracks are observed due to higher loss in structural water. The mullitisation behavior is confirmed by XRD and microstructural analysis. Even though the XRD results confirm the mullitisation, the high peak intensity is observed only for pure and fine particle size alumina source (Neyveli clay and alumina) samples. The microstructure of the above samples clearly confirms the presence of maximum amount of mullite. The impurities present in gibbsite make the mullite crystal shapes imperfect, especially in the impure Udayarpalayam clay. Though the physical properties are poor for boehmite samples, the microstructure confirms that better lengthy mullite crystals are formed.

#### 4. Conclusion

The following conclusions are drawn from the results of the present investigation.

1. Pure Neyveli clay and fine alumina yield better mullite crystals with good physical properties.
2. The mullite prepared using gibbsite shows that the presence of a higher amount of secondary mullite crystals than the primary crystals due to the presence of impurities.
3. The mullite prepared using boehmite has poor mechanical strength though the aspect ratio of the mullite crystals is maximum.
4. The impurities in the raw materials improve the strength but not density in mullite formation.
5. No crystalline silica is observed for the sample prepared at 1600 °C.

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