

Effect of size of fly ash particle on enhancement of mullite content and glass formation

PARVEEN SULTANA, SUKHEN DAS*, BISWAJOY BAGCHI,
ALAKANANDA BHATTACHARYA[†], RUMA BASU^{††} and PAPIYA NANDY

Department of Physics, Jadavpur University, Kolkata 700 032, India

[†]Department of Physics, West Bengal State University, Barasat, India

^{††}Department of Physics, Jogamaya Devi College, Kolkata 700 026, India

MS received 17 August 2009

Abstract. Quartz is widely replaced by fly ash in traditional porcelain composite. Increased strength and stability of the fly ash-mixed composite depends on the quantity and crystallinity of the mullite phase in the fly ash. Our aim in this investigation is to increase the formation of mullite in nanocrystalline form and study the effect of temperature. Quantitative estimation of mullite and residual quartz content were done by X-ray diffraction (XRD) and nanostructure and crystallization were studied using differential thermal analysis (DTA), field effect scanning electron microscopy (FESEM), XRD and Fourier transform infrared (FTIR) spectroscopy. The results show that fly ash sieved through 250 holes/cm² mesh contain more mullite initially and growth of mullite as well as glass formation was faster in this sample compared to coarse fly ash. The maximum mullite in these samples was formed at 1600°C. Transformation of quartz and cristobalite phases into glassy phase was also faster for smaller particle sizes of fly ash.

Keywords. Fly ash; mullite; composites; spinels; X-ray methods.

1. Introduction

Fly ash is a waste product produced from thermal power stations during the combustion of pulverized coal containing mainly SiO₂ and Al₂O₃ (Cioffi *et al* 1994; Belardi *et al* 1998). Increased generation of electricity through the thermal route involving combustion of pulverized coal leads to huge production of fly ash and is in fact a matter of great concern (Pandian and Krishna 2003). Scientists around the world are aiming at gainful utilization and disposal of fly ash. Fly ash is some times used in buildings, construction of roads, embankment and cement industries (Yeledhalli *et al* 2007). A large amount of fly ash is used as a fine aggregate to substitute for Portland cement in concrete. Because of the presence of SiO₂ and Al₂O₃ in high proportions in fly ash, it is used to synthesize mullite. Mullite is an important and widely studied ceramic material. It is used in a diverse number of applications, including structural and refractory ceramics, microelectronic packaging, high-temperature protective coatings, microwave dielectrics and infrared-transmitting materials (Okada *et al* 1991; Somiya and Hirata 1991; Kansal *et al* 1997; Soundararajan *et al* 2001; Hongping *et al* 2004). Mullite is an attractive ceramic for high-

temperature structural application as it has high creep resistance, low thermal expansion coefficients and good chemical and oxidation resistance (Ohira *et al* 1991; Schneider *et al* 1994).

In our previous work, we observed that substitution of quartz by fly ash in a normal porcelain body increases its flexural strength and density and decreases its porosity in the entire temperature range. Flexural strength increase may be due to the formation of small size secondary mullite needle, which gets embedded in the glassy matrix (Kumar *et al* 2001; Dana *et al* 2004).

In our present work, our aim is to observe the presence of mullite and quartz in raw fly ash and their qualitative and quantitative changes in the entire temperature range based on their different particle sizes. Three different coal fly ash samples were collected from different thermal power stations and screened through different meshes (50, 100, 200, 250 holes/cm²). Fly ash is a combustion product containing mullite needle and quartz phase, which is an essential criterion for a filler material in porcelain composition. From the experimental data, we observed that mullite content increases with decreasing particle size of fly ash, as the surface area increases with decreasing particle size. Maximum mullite is found from the samples passing through 250 holes/cm² mesh. Mullite formation also increases after thermal treatment at 1000, 1200, 1400 and 1600°C. Experimental data indicate that both the rate of

*Author for correspondence (debasis35@yahoo.co.in)

Table 1. Labelling of 12-fly ashes.

Name (holes/cm ² mesh)	Sample I	Sample II	Sample III
50	FA1-50	FA2-50	FA3-50
100	FA1-100	FA2-100	FA3-100
250	FA1-200	FA2-200	FA3-200
250	FA1-250	FA2-250	FA3-250

mullite formation and amount of mullite were maximum in the low particle size sample. The mullite formed in such sample is highly crystalline but in the nano form. Transformation of quartz and cristobalite phases into glassy phase is also faster in smaller particle size of fly ash.

2. Experimental

2.1 Materials

Three commercially available fly ashes (FA1, FA2 and FA3) were collected for investigation from different thermal power plants in India.

2.2 Sample preparation

Three different fly ash samples were sieved through 50, 100, 200 and 250 holes/cm² mesh. A total of 12 fly ash samples were named as in table 1, based on their batch number and particle size number. The fly ash samples, separated by sieving, were fired in a furnace at a rate of 5°C/min to maximum temperatures of 1000, 1200, 1400 and 1600°C with 2 h soaking time and cooled normally. After cooling, the samples were ground and finally stored for different analyses.

2.3 Characterization

2.3a X-ray diffraction: All samples were analysed in X-ray diffractometer (Model D8, Bruker AXS), attached with primary and secondary monochromators and a computer. The tube was operated at 40 kV/40 mA, CuK α radiation of 1.5418 Å. The instrument was run at scan mode with increment of 0.02 and scan speed of 5 s/step, within the angle range 10–70° (2θ range).

The lattice parameters, crystal size and strain were calculated step by step after refinement of the raw data. Software programs such as Profit, Diccult, Quasor and itos based on various mathematical and statistical methods were used in this correction and calculations. The raw data was refined with respect to 2θ correction, peak asymmetry, change in full-width at half-maximum (FWHM), unit cell parameters using Quasor and Profit-software programs. Diccult and itos were used to refine the crystal structure parameters. The crystal size of mullite was obtained from refined data with the help of line

broadening method, initially described by Alexander and Klug (1954) and later corrected by Debye–Scherrer. Here the diameter of the crystallites, D is related to the λ , the wavelength of CuK α line, β , the FWHM in radians and θ , the Bragg angle by the following equation:

$$D = (0.9\lambda)/(\beta \cos\theta).$$

Corrected $\beta = \sqrt{(\beta_0)^2 - (b)^2}$ where, β_0 is the FWHM in radians for the sample and b the FWHM in radians for the pure crystal.

Quantitative analysis and strain calculation were done from the refined data with the help of Rietveld analysis, where preferred orientation, atomic displacement factor, among others, were taken into consideration.

2.3b Fourier transform infrared spectra: The FT–IR spectra of samples were measured by FT–IR spectroscopy (FTIR-8400s, Shimadzu) with 200 scans for wavenumber ranging from 400 to 2000 cm⁻¹ to study their structural features. The KBr pellet method was used to prepare the samples (Oréface and Vasconcelos 1997).

2.3c Morphological analysis by scanning electron microscopy: The morphological structure of raw fly ashes and thermally treated fly ashes were obtained using scanning electron microscopy (SEM).

2.3d Surface area: BET (Brunauer–Emmett–Teller) method was used to measure the specific surface area of the samples using area-meter II by nitrogen gas absorption in a flow rate 4.5 l/h.

3. Results and discussion

3.1 Sequential changes of three fly ashes

Fly ash is a burnt material. So the presence of mullite and quartz phases were detected by XRD. These XRD patterns confirm that the amount of mullite increases as particle size decreases (figure 1). The same results were observed among the different three types of fly ashes, where maximum mullite is obtained from the fly ash sample passed through 250 holes/cm² mesh. The amount of mullite present is based on different particle sizes in three different fly ashes is shown in figure 1(d).

Using BET method, the surface area was measured, which gradually increased with the smaller particle size.

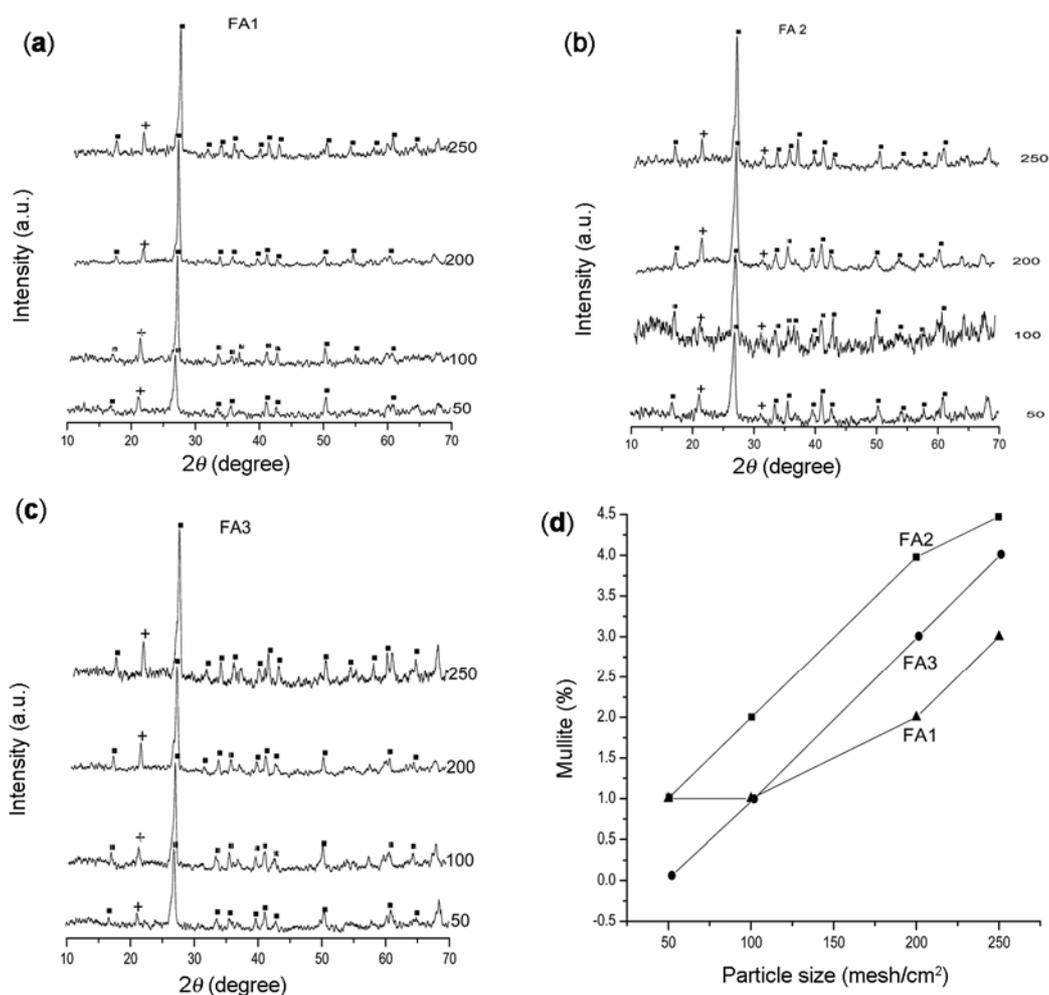


Figure 1. (a)–(c) are XRD pattern of original fly ash samples of different particle sizes. (d) Increase of mullite with particle size in FA1, FA2, FA3 raw samples (•, mullite; +, quartz).

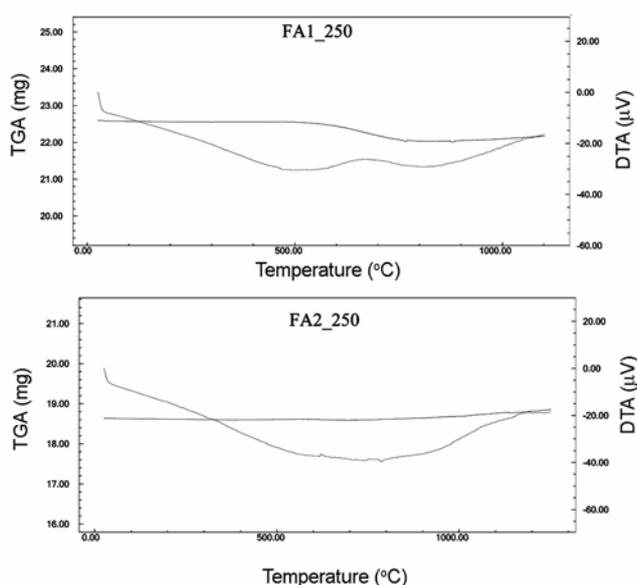


Figure 2. DTA curves of original fly ash samples.

Formation of high-temperature phases obtained upon heating was monitored by XRD in all samples. The kinetics of the reaction upon heating as observed by differential thermal analysis (DTA) and thermal gravimetric analysis (TGA) curve (figure 2) indicates a very little weight loss through a continuous endothermic reaction. As this is a burnt material, there is no sharp peak or peak due to spinel formation.

Within the temperature 1000°C, there were no noticeable changes in the phases within the samples. XRD pattern (figure 3) indicates very little, but clearly the poor crystalline growth of the mullite. Evaporation due to humidity and other materials causes weight loss. The growth of mullite is faster in smaller particle size of fly ash due to larger surface area. The X-ray pattern indicates the presence of large amount of quartz.

At 1200°C, XRD peaks corresponding to mullite became more prominent indicating the growth of the mullite. Peaks are still broad, indicating poor crystalline mullite. Flatness of the 1170 cm⁻¹ peak of FTIR (figure 6) also

confirms the poor crystallization of the mullite. The amount of quartz decreases a little and the cristobalite phase appears in the all samples.

At 1400°C, XRD pattern of mullite indicates the increase in intensity and decrease in broadness of mullite peaks, i.e. growth of mullite as well as increase in crystal size. But the growth of mullite within this temperature range is not same for the samples of different particle sizes especially growth is much higher for the particle of smaller size (250 holes/cm² mesh) (figure 4a) and the crystal size also increases (figure 4c). FTIR analyses were also indicating the quick crystallization of all the three samples, i.e. FA1-250, FA2-250 and FA3-250. Intensity of quartz peak decreases and a small glass band was observed. The amount of quartz decreases much faster and the existence of the glassy phase and cristobalite phase became much prominent in all the samples, especially in FA3 samples.

At 1600°C, the intensity of mullite peaks become sharper in all samples. Crystal size, crystal strain, FTIR analysis and FESEM study indicate the complete crystallization of mullite in all samples and their nano form. The amounts of quartz and cristobalite decrease much and decay completely in FA3, which transform into glassy phase, and so the glass band becomes prominent.

3.2 Mullite formation

3.2a *Semi-quantitative analysis of mullite formation:* XRD pattern (figure 1) indicates the presence of mullite

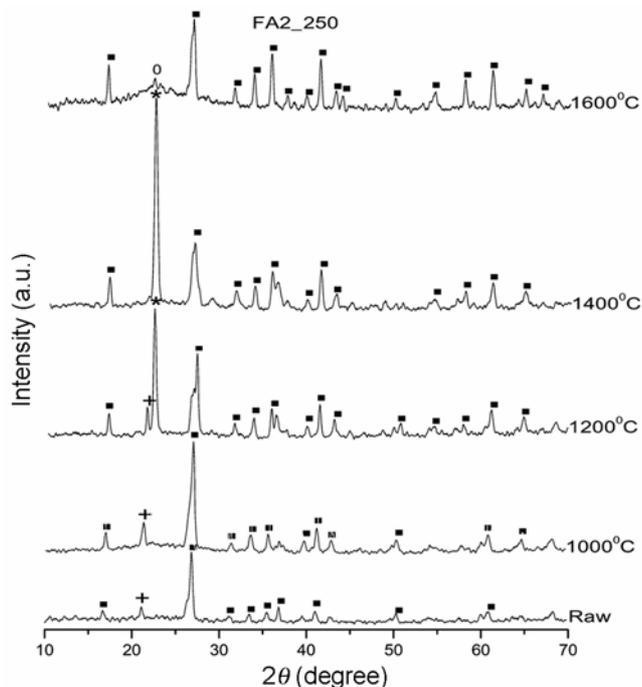


Figure 3. XRD pattern of 250 particle sized sample fired at different temperatures. (., mullite; +, quartz; *, cristobalite; 0, glass.)

and quartz phases in all fly ashes as it is a burnt material. Mullite formation starts very slowly above 1000°C without any sharp transition indicated by DTA/TGA (figure 2). Upon heating, the mullite formation increases. It increases to a considerable amount on heating to 1400°C for finer fly ash and 1600°C for coarse fly ash. All three fly ashes follow the same growth path. At 1600°C mullite formation become more or less constant on further heating (figure 4b).

Crystal size measured from XRD pattern using line broadening method described by Klug and Alexander indicates the sizes within 17–35 nm range. FESEM analysis (figure 6) also supports the calculated crystal size.

To measure the crystalline parameters *a*, *b* and *c*, initially Brindley and Nakahira (1959) used single crystal of clay treated to different temperatures and found that in the temperature range 1200–1400°C, both *a* and *c* decrease and *b* remains unaltered. Cameron (1977) also published similar data. He noted that a cell parameter showed greatest change with alumina content. The plot of *a* vs Al₂O₃ composition was found to be linear. Mazdiyasi *et al* noted a two-step formation curve of mullite. In the first step, primary mullite was formed where *a*-axis length decreased with increasing temperature in the lower temperature region. In the second step when secondary mullite was formed, *a*-axis remained constant with increasing temperature. According to them, the first step corresponds to tetragonal-like mullite and second one corresponds to alumina-rich 3 : 2 mullite.

As fly ash is a burnt material, primary mullite is present in the initial fly ash and the percentage of mullite was higher in smaller sized fly ash due to more surface area. Upon heating up to 1200°C, a further growth of primary mullite was observed, which is more in the smaller particle-sized fly ash and very low in bigger particle sized fly ash. Due to large surface area, complete primary formation took place in finer particle size. The growth of mullite formation suddenly increases to a considerable amount above 1200°C, where secondary mullite formation takes place. The growth rate is maximum in smaller size due to the larger surface area where as it is rather slow in big sized fly ash particles (figure 4b) due to less surface area.

3.3 Change of crystalline size and lattice parameters of mullite

The effect of heat treatment on the change of size of mullite is shown in figure 4c. Upon heating, as the growth of mullite formation was faster for finer fly ashes, the crystal size also increases at a faster rate. Similarly as the growth of mullite is slower for bigger sized fly ash particles, crystallization was also slower in this case. Maximum crystal size was obtained in the sample of 250 holes/cm² mesh. Changes in lattice parameter of mullite are shown in figure 5.

The lattice constant values change with temperature on heat treatment (Schneider *et al* 1993). Out of three

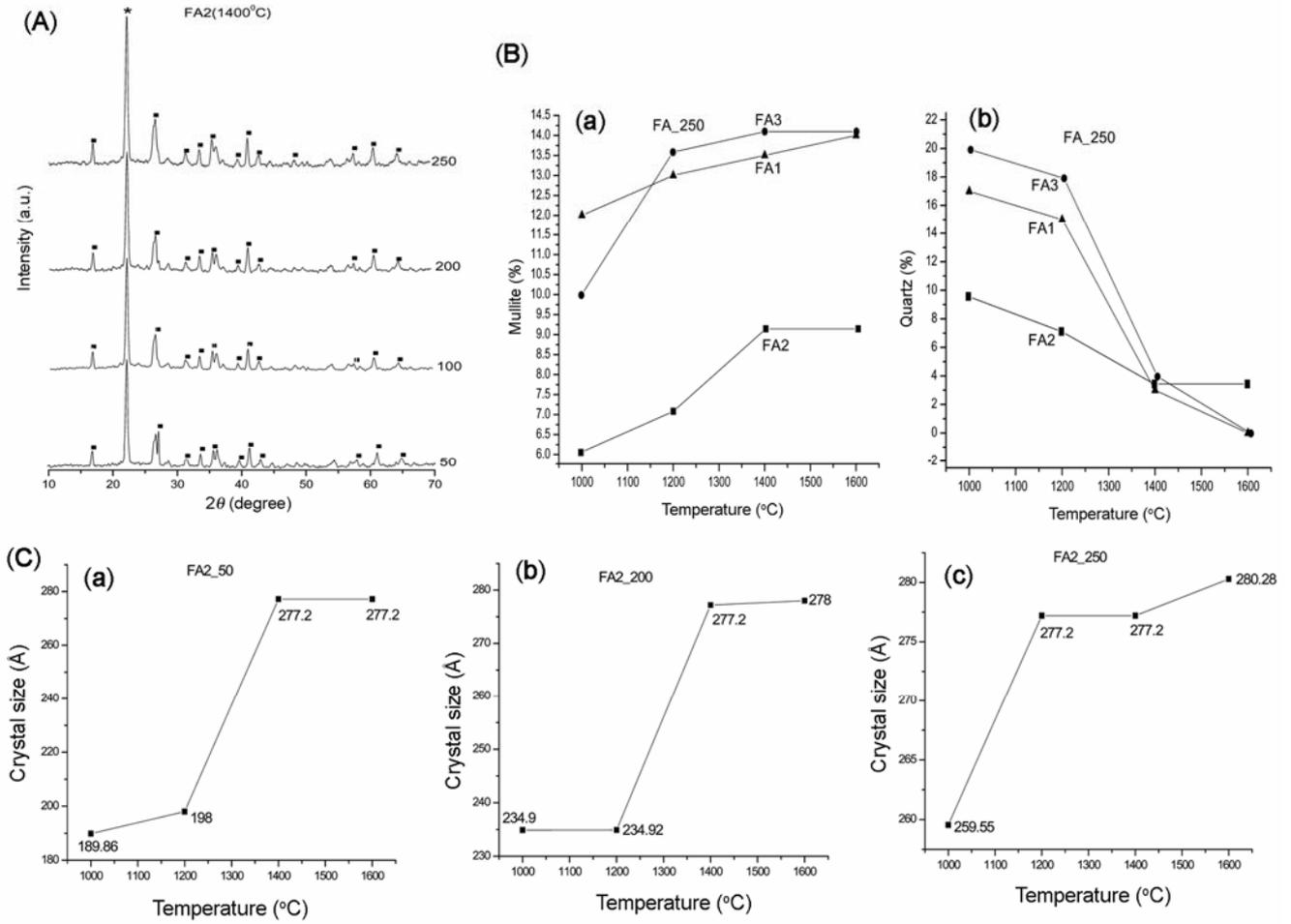


Figure 4. (A) XRD pattern of 1400°C heated sample of different particle sizes. (., mullite ; *cristobalite). (B) Variation in the growth of mullite (a) and the formation of quartz (b) with respect to heating temperatures. [▶, FA1; ■, FA2; ●, FA3]. (C) Growth of mullite shown according to different crystal sizes produced from thermally-treated fly ash samples at different temperatures of (a) 50, (b) 200 and (c) 250 particle sizes.

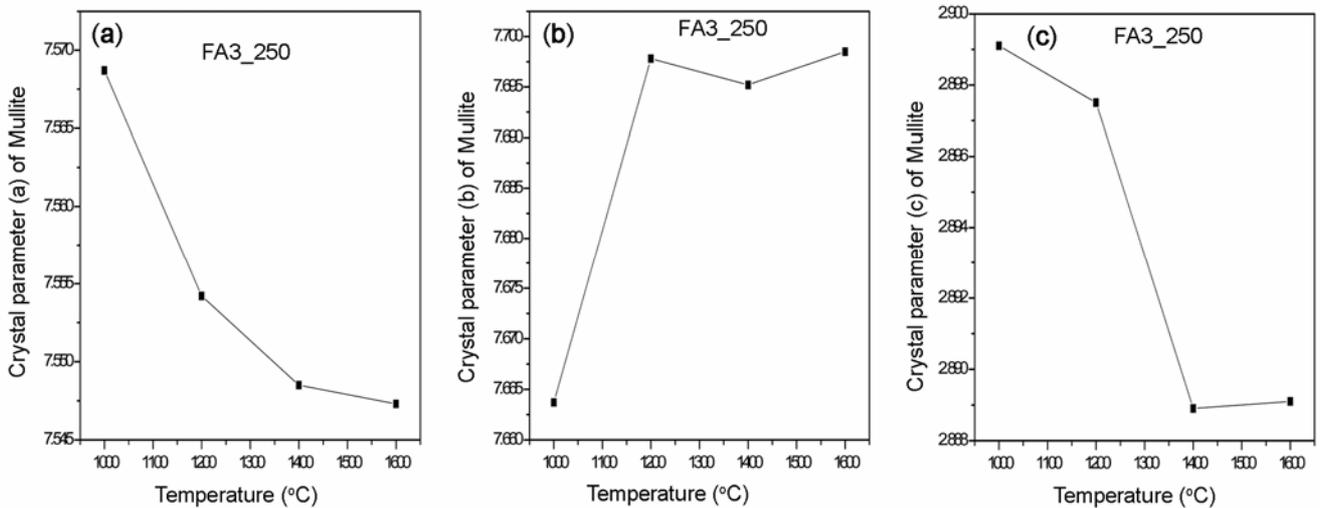


Figure 5. Variation in crystal parameter of mullite with heating temperature. (a) *a*-axis, (b) *b*-axis and (c) *c*-axis.

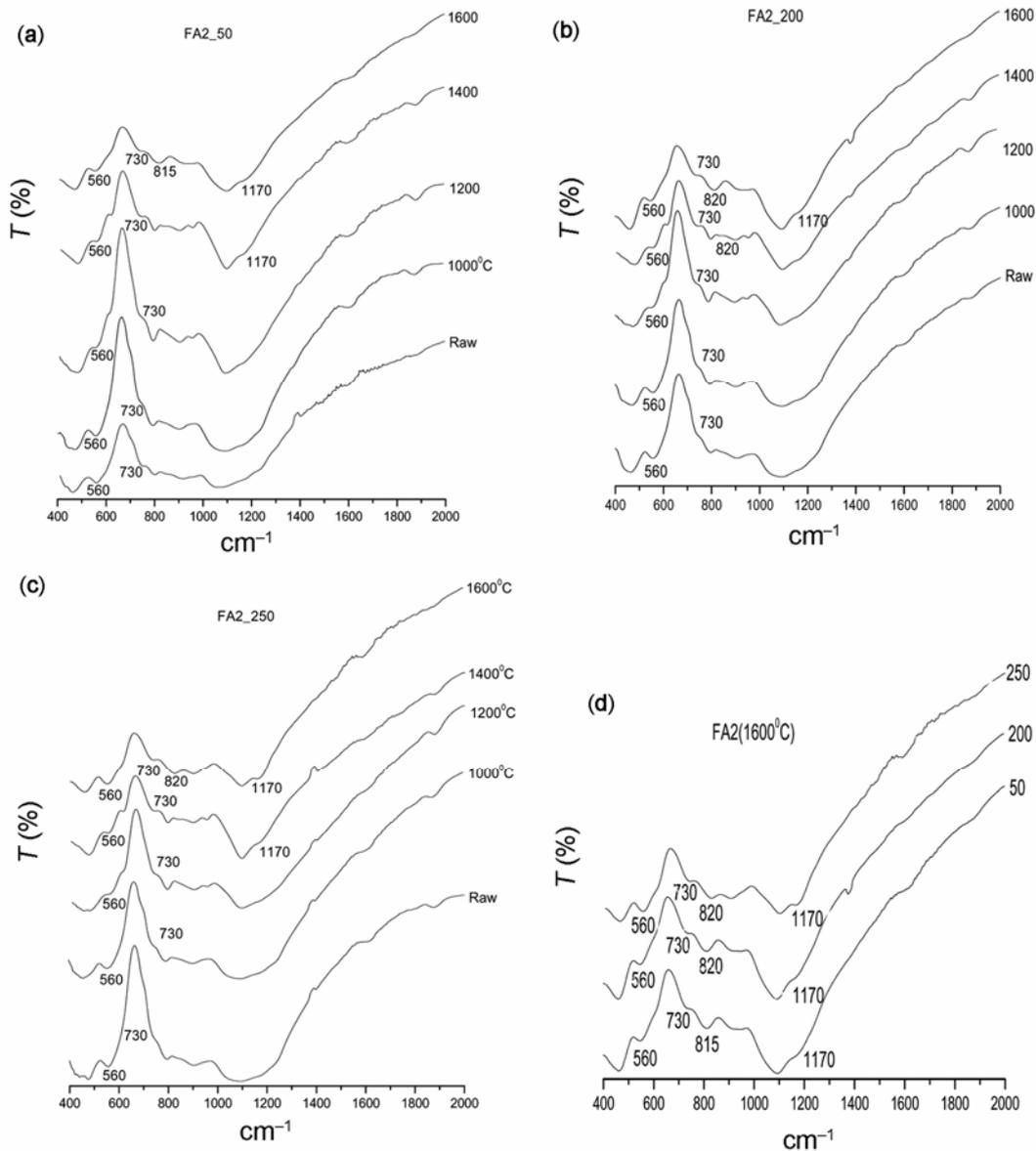


Figure 6. (a–c) FTIR spectra of mullite prepared from original fly ash and thermally-treated fly ash of different particle sizes at different temperatures. (d) Variation in mullite formation represented by the sharpness of peak with various particle sizes at 1600°C.

parameters, the a -axis decreases rapidly from 7.5687 nm at 1000°C to 7.5542 nm at 1200°C for FA3, after which the change is lower. Other samples also follow a similar pattern. The b -axis initially increases from 7.6637 to 7.6978 nm for FA3 at 1000–1200°C and thereafter, the value becomes constant up to 1600°C. Similarly, c -axis decreases rapidly within the temperature range of 1000–1200°C and then varies very slowly. Other samples also follow a similar pattern.

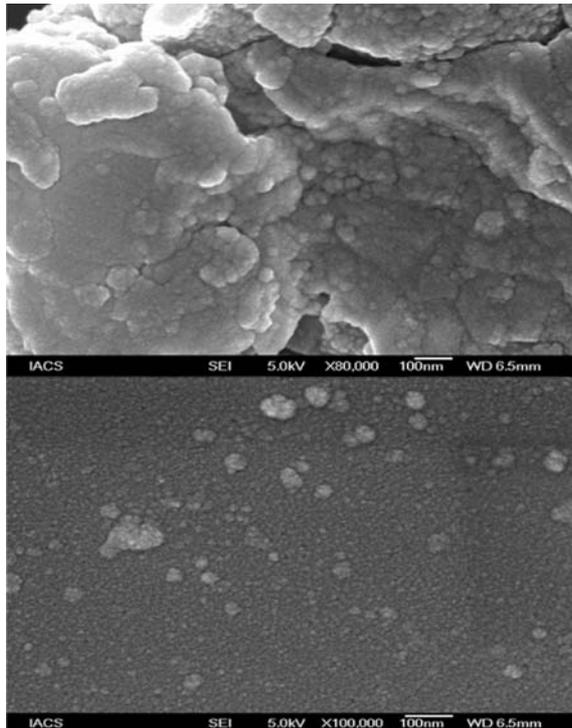
3.4 FTIR

The Fourier transform infrared spectroscopic results of the original fly ash and heat-treated fly ash are shown in figure 6.

Peaks associated with mullite appear at around 560 and 730 cm^{-1} . These peaks correspond to alumina octahedra and alumina tetrahedra, respectively. Both the peaks are present in original fly ash as well as in the thermally treated fly ashes but the bands associated with silica tetrahedra and alumina tetrahedra, respectively at around 1170 and 820 cm^{-1} are found when the sample was treated at 1400 and 1600°C. The presence of mullite is responsible for a series of bands at around 560, 730, 820 and 1170 cm^{-1} . At 1600°C, mullite gives sharp peak due to the well-crystallized mullite, which occurs in all the cases. From the curves, it is also clear that the sample passed through 250 holes/ cm^2 mesh show the maximum sharpness and crystallinity of mullite compared to others as the surface area increases.

Table 2. Results of surface area analysis of original and thermally-treated fly ash.

Original sample	Surface area (m ² /g)	Thermally-treated sample	Surface area (m ² /g)
FA-50	2.97	FA-250 (1200°C)	4.0
FA-200	4.30	—	—
FA-250	4.34	FA-250 (1600°C)	3.5

**Figure 7.** Field emission scanning electron micrographs.

3.5 FESEM

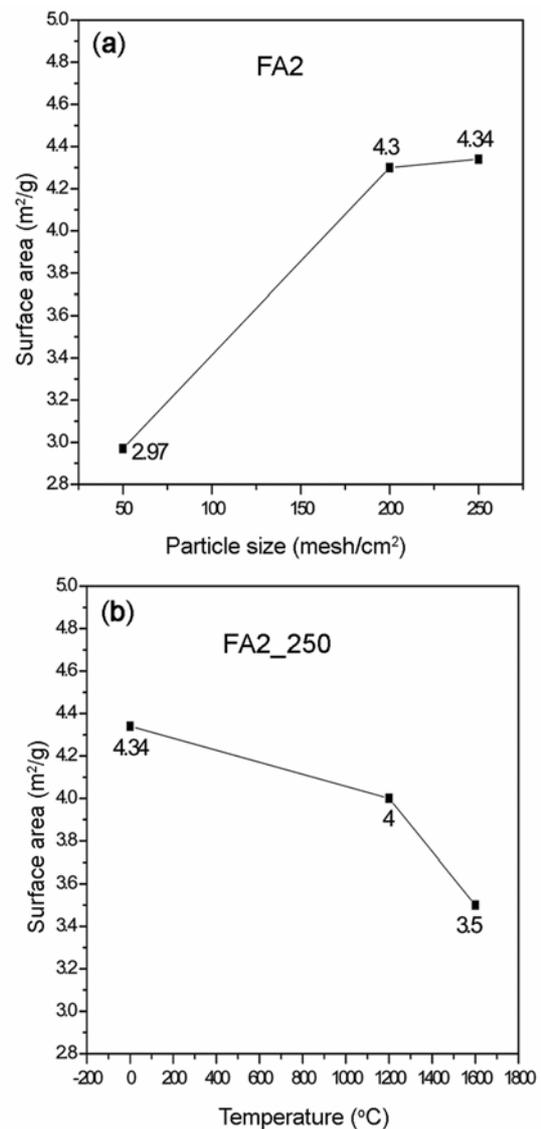
The FESEM (JSM6700F JEOL Ltd, Tokyo, Japan) of the thermally-treated fly ash is shown in figure 7.

The micrographs of 250 cm²/hole particle sized sample fired at 1600°C reveal the presence of mullite of definite crystal size.

3.6 BET method

The surface area of the sample was determined by the BET method using area-meter II by nitrogen gas absorption and the results are given in table 2.

According to table 2 and figure 8, it is established that surface area increases with decreasing particle size and decreases with increasing temperature. Maximum surface area is observed in the sample sieved through 250 holes/cm² mesh. At 1600°C, for small particle-sized sample, the surface area is minimum due to good crystallinity.

**Figure 8.** Variation of specific surface area of (a) 50, 200, 250 particle sized samples and (b) thermally-treated samples.

4. Conclusions

(I) The mullite content increases with decreasing particle size of fly ash as the surface area increases. Maximum mullite is found for the samples passing through 250 holes/cm² mesh.

(II) Mullite formation increases after thermal treatment at 1000, 1200, 1400 and 1600°C. Experimental data indicate that for thermally-treated samples, both the rate of mullite formation and maximum amount of mullite formed in low particle-sized sample. The mullite formed in such a sample is completely crystalline and in nano form.

(III) Transformation of quartz and cristobalite phases into a glassy phase is also faster in smaller particle-sized fly ash.

From our experimental observations, we may conclude that smaller sized fly ash particle will form nano-crystalline mullite at lower temperature. Thus, smaller-sized fly ash particle into porcelain increases the percentage of mullite formation at relatively low temperature (1400°C) and mullite in nano form also mixes well in ceramic matrix. Thus incorporation of fly ash leading to mullite formation increases the strength of porcelain and hence a new economically viable proposition.

Acknowledgement

We are grateful to University Grants Commission (UGC), Government of India, for financial assistance.

References

- Alexander I F and Klug H P 1954 (New York: Wiley) Ch 7
- Belardi G et al 1998 *Conserv. Recycling* **24** 167
- Brindley G W and Nakahira M 1959 *Am. Ceram. Soc.* **42** 315
- Cameron W E 1977 *Am. Ceram. Soc. Bull.* **56** 1003
- Cioffi R, Pernice P, Aronne A, Catauzo M and Quattroni G 1994 *J. Eur. Ceram. Soc.* **13** 143
- Dana K, Das S and Das S K 2004 *J. Euro. Ceram. Soc.* **24** 3169
- Hongping H et al 2004 *Spectrochim. Acta Part A: Mol. Biomol. Spectrosc.* **60** 1061
- Kansal P and Laine R M 1997 *J. Am. Ceram. Soc.* **80** 2597
- Kumar S, Singh K K and Rao P R 2001 *J. Mater. Sci.* **36** 5917
- Mazdiyasn K S and Brown L M 1972 *J. Am. Ceram. Soc.* **55** 548
- Ohira H et al 1991 *J. Mater. Sci. Lett.* **10** 847
- Okada K, Otsuka N and Somiya S 1991 *Am. Ceram. Soc. Bull.* **70** 1633
- Orefice R L and Vasconcelos W L 1997 *J. Sol-Gel Sci. Technol.* **9** 239
- Pandian N S and Krishna K C 2003 *J. Test. Evaluat.* **31** 479
- Schneider H, Okada K and Pask J 1994 *Mullite and mullite ceramics*
- Schneider H, Rodewald K and Eberhard E 1993 *J. Am. Ceram. Soc.* **76** 2896
- Somiya S and Hirata Y 1991 *Am. Ceram. Soc. Bull.* **70** 1624
- Soundararajan R, Kuhn G, Atisivan R, Bose S and Bandyopadhyay A 2001 *J. Am. Ceram. Soc.* **84** 509
- Yeledhalli N A et al 2007 *J. Agric. Sci.* **20** 531