

MULLITE FORMATION IN COAL FLY ASH IS FACILITATED BY THE INCORPORATION OF MAGNESIUM OXIDE

Parveen Sultana¹, Sukhen Das¹, Alakananda Bhattacharya², Ruma Basu³ and Papiya Nandy¹

¹Physics Department, Jadavpur University, Kolkata- 700032, India

²Physics Department, West Bengal State University, Barasat, WB, India

³Physics Department, Jogamaya Devi College, Kolkata- 700026, India

Received: June 30, 2010

Abstract. We have studied the chemical and mineralogical composition of different coal fly ash samples, collected as byproducts from thermal power plants. With the addition of magnesium oxide (MgO), the percentage of mullite increased when the fly ash samples were sintered at 1600 °C. X-ray diffraction (XRD) results revealed that mullite, cristobalite and corundum were the main phases of the sintered fly ash. With an increase in MgO content, the peak intensity of mullite and corundum increased while that of cristobalite decreased.

1. INTRODUCTION

Mullite, ideally $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, is a high-melting crystalline aluminosilicate material which has long been used in heavy-duty refractories [1]. The unique mechanical and thermal properties of mullite such as high refractoriness, low thermal conductivity, low thermal expansion, good chemical stability, and its interesting mechanical properties at high temperature, make it a promising engineering material. In the last decade, the need to produce high quality mullite for optical, dielectric and structural applications has led to numerous studies on the synthesis and processing of mullite [2-6].

Fly ash, an easily available byproduct of thermal power stations, contains about 10% mullite, as well as other oxides such as silica, alumina, calcium oxide, iron oxide and alkali oxides [7,8].

We have shown here that mullite production in coal fly ash can be enhanced from 10% to 39% by incorporating magnesium oxide (MgO) (Merck), thereby facilitating its use in the ceramic industry. Considering the easy availability of the raw materi-

als and production costs, MgO-treated fly ash should prove a very promising material for use in glass-ceramic production. Fly ash exists as a fine dust, and so it can be directly incorporated into ceramic pastes as a raw material resource [9-16].

2. MATERIALS AND METHODS

2.1. Sample preparation

Coal fly ash samples (FA1, FA2) were collected from two different Indian thermal power plants. These samples contained both amorphous components (mainly SiO_2 , Al_2O_3) and crystalline components (mainly quartz and mullite). Metal oxides of Fe, Ti, Ca, Mg, K, etc., and some oxides of trace elements like Sr, Ba, Zr, etc, were also present in these samples, as shown in Table 1.

The samples were sieved through 250 holes/cm² mesh and washed several times. The samples were then homogeneously mixed with 1, 3, and 5% (w/w) of magnesium oxide (MgO) by dry milling for 4 hours and subsequently wet milling in a ball mill at 1200 rpm for 40 minutes. The mixed samples were then

Corresponding author: Sukhen Das, e-mail: das_sukhen@yahoo.com

Table 1. Chemical analysis of Fly Ash (% w/w).

Element	Sample 1 (FA1)	Sample 2 (FA2)
O	23.88	37.44
C	45.34	3.60
Si	15.14	29.03
Al	7.76	17.65
Fe	3.52	4.11
Ti	1.32	2.46
Ca	0.60	0.92
Mg	0.29	1.18
V	0.22	1.28
Na	0.20	0.30
K	0.89	1.19
Zr	1.43	1.78
Ba	2.63	0.111

dried at 70 °C for 48 hours in an oven. The samples were fired at 1600 °C in an electric furnace with a heating rate of 5 °C/min and 120 min of soaking time. After cooling, the samples were ground in an agate mortar to a fine powder form and finally stored at room temperature for different analysis.

2.2. Characterization techniques

The fired samples of FA1 and FA2 were subjected to characterization by X-ray diffraction (XRD) (Model D8, Bruker AXS) to determine the crystallinity of the sample, using CuK α radiation at 1.540 9Å ($2\theta = 10^\circ$ -70°, scan speed = 0.2 s/step, increment = 0.02, operating voltage = 40 kV and operating current = 40 mA). The crystalline phases were identified by comparing peak positions and intensities (finger print method).

The thermal reaction processes (i.e. different phase transition temperatures including mullitization temperatures) were measured using a dynamic thermal analyser/thermogravimetric analyser (DTA/TGA) (DTG-60H, Shimadzu) instrument. The DTA/TGA analysis was performed on both the untreated fly ash sample and the MgO-treated sample, in an N₂ gas atmosphere.

To determine the structural features of all the samples, Fourier transform infrared (FTIR) spectroscopy was carried out using an FT-IR spectrometer (FTIR-8400s, Shimadzu), with 200 scans for wave numbers ranging from 400-2000 cm⁻¹ and resolution 4 cm⁻¹. The KBr pellet method was used to prepare the samples [17].

To investigate the morphological structure of sample surfaces, surface textures were examined

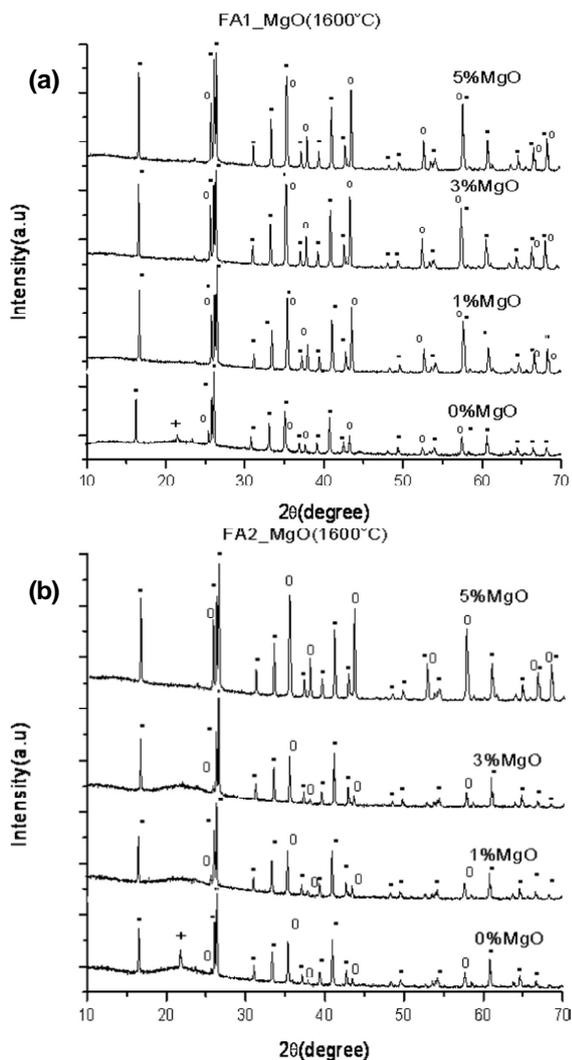


Fig. 1. X-ray diffraction pattern of untreated and MgO-treated fly ash samples, (a) FA1 and (b) FA2, sintered at 1600 °C for 2 hrs. [■, mullite; +, cristobalite; 0, corundum].

by field emission scanning electron microscopy (FESEM) (JSM6700F JEOL LTD, Tokyo, Japan), and energy dispersion X-ray fluorescence spectroscopy (EDAX) (FEI QUANTA 200) was also carried out.

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction (XRD) analysis

Fly ash is a burnt material, and contains high amounts of silica; the XRD analysis confirmed the presence of SiO₂ in cristobalite form and a small amount of mullite in untreated fly ash samples sintered at 1600 °C (Fig. 1). The sharp peak of

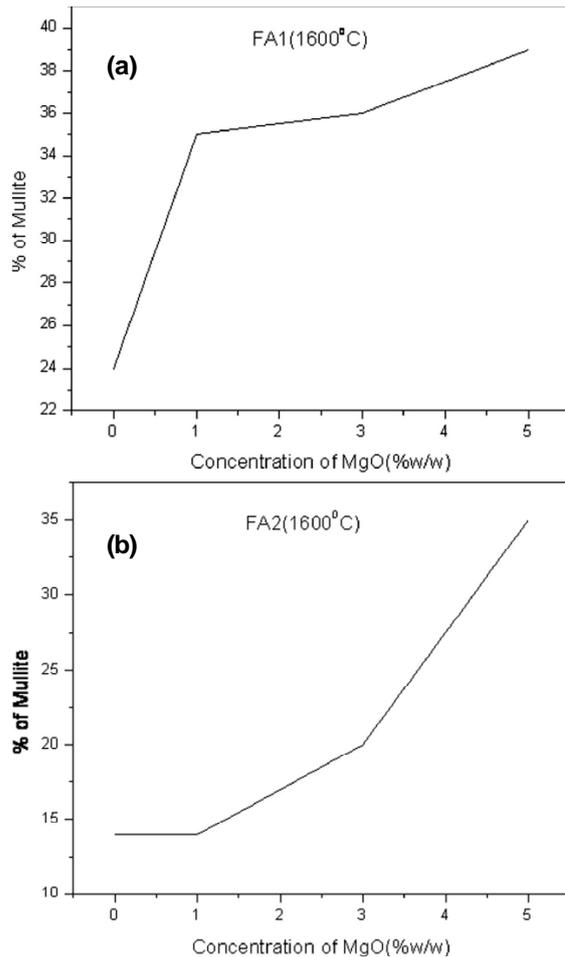


Fig. 2. Relative growth of mullite developed from fly ash samples, (a) FA1 and (b) FA2, with respect to different concentrations of MgO at 1600°C.

cristobalite was more prominent in FA2 compared to FA1.

Mullite grains continued to grow with increasing concentrations of MgO from 1 to 5% w/w. The maximum degree of mullitization was observed for 5% w/w MgO at 1600 °C (Fig. 1). The collected data were refined using Profit software. Topaz and Quasor software based on Rietveld were used to calculate the percentage of mullite in untreated and MgO-treated samples of FA1 and FA2 sintered at 1600 °C (Fig. 2), where standard mullite was used as a reference material.

The result indicated that the presence of MgO lowered the activation energy of the reaction system and enhanced the reaction rate of Al_2O_3 - SiO_2 to form mullite. The acceleration of mullite crystal growth was probably due to the significant decrease in the viscosity of the glassy phase due to the fluxing effect of MgO [18-22].

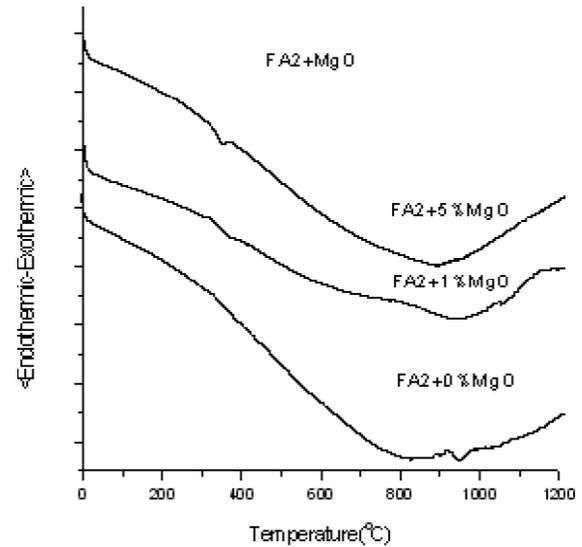


Fig. 3. DTA curves of the untreated and MgO-treated fly ash samples.

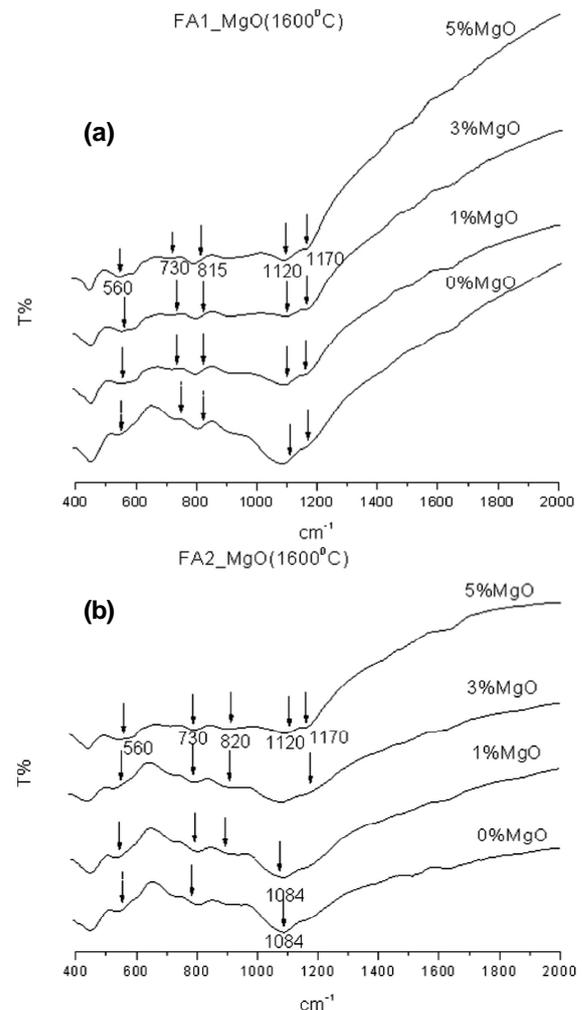


Fig. 4. FTIR spectra of untreated and MgO-treated fly ash samples, (a) FA1 and (b) FA2, sintered at 1600 °C for 2 hrs.

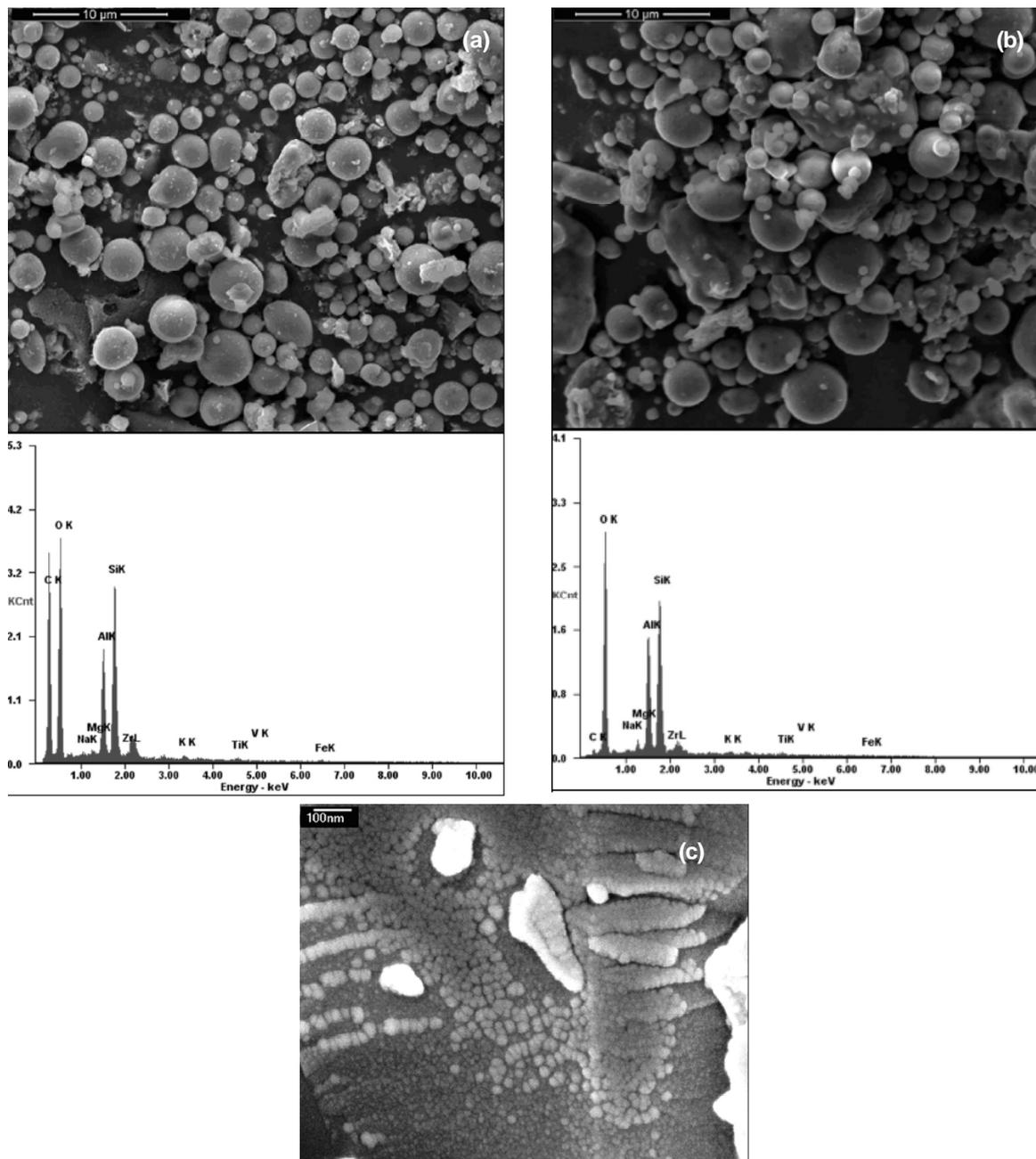


Fig. 5. FESEM/EDAX of the untreated samples, (a) FA1, (b) FA2; FESEM of 5% w/w MgO-treated FA2 sintered at 1600 °C, (c).

3.2. DTA-TG analysis

The DTA analyses of the untreated and the MgO-treated samples of fly ash (Fig. 3) show a slow endothermic fall within the temperature range. In both cases the fall was due to the evaporation of water absorbed in the samples. As the fly ash is already a burnt material and contains a small amount of mullite, no such detectable change was observed in DTA. In Fig. 3 the DTA analysis of only FA2 was

shown, FA1 showed the same result. Whereas the TGA analyses of the untreated and the MgO-treated samples of fly ash (not shown in figure) show a small weight loss.

3.3. Fourier transform infrared (FTIR) studies

In the FTIR analysis of the FA2 samples sintered at 1600 °C (Fig. 4b), bands associated with mullite

appear at around 560 cm^{-1} and 730 cm^{-1} . These two bands correspond to alumina octahedra (AlO_6) and alumina tetrahedra (AlO_4) respectively. Both these bands are present in the untreated fly ash as well as in the MgO-treated fly ashes but the bands characterizing silica tetrahedra (SiO_4) and alumina tetrahedra at around 1170 cm^{-1} and 820 cm^{-1} respectively were found only upon increasing MgO concentration. An additional band at around 1120 cm^{-1} , corresponding to silica tetrahedra, was observed only for 5% concentration. At $1600\text{ }^\circ\text{C}$, as the concentration of MgO increases, mullite gives a sharp band due to the well crystallinity of mullite, and this occurs in all cases. Since FA2 contains large amounts of quartz, as detected by XRD, a band at around 1084 cm^{-1} corresponding to cristobalite appears in the untreated sample and the 1% MgO-treated sample. This band disappears with increasing MgO concentration.

In the FTIR analysis of the FA1 samples sintered at $1600\text{ }^\circ\text{C}$ (Fig. 4a), all the bands at around 560 cm^{-1} , 730 cm^{-1} , 820 cm^{-1} , 1120 cm^{-1} , and 1170 cm^{-1} appear both in untreated and in MgO-treated fly ash samples. The sharpness of the bands increases with increasing concentration of MgO. These are characteristic mullite phase bands as reported by Oreifice and Vasconselos [23]. From Fig. 4 it is also clear that the samples treated with higher concentrations of MgO show the maximum sharpness and crystallinity of mullite. The band of 1084 cm^{-1} corresponding to cristobalite is not detectable in the untreated FA1 sample, since it contains only a very small amount of cristobalite.

3.4. FESEM analysis

Figs. 5a and 5b show the FESEM/EDAX results for untreated FA1, FA2 samples, respectively. The micrographs indicate that the untreated fly ash consists of spherical particles and that the particle surface is very smooth, but with several cracks. Fig. 5c shows the FESEM result for the FA2 sample treated with MgO 5% w/w. The micrograph reveals the presence of prominent, large, spherical, well-crystalline mullite particles. A similar result was obtained for the MgO-treated FA1 sample.

4. CONCLUSIONS

Our results indicate that the percentage of mullite in fly ash can be significantly enhanced by treating the fly ash with small amounts of magnesium oxide (MgO). Two types of fly ash (FA1 and FA2), with

different chemical compositions, were investigated. A significant reduction in the peak intensity of the cristobalite phase and a significant increase in mullite arise following the introduction of 1 to 5% w/w MgO. The presence of MgO in fly ash leads to accelerated mullite formation during the sintering process at $1600\text{ }^\circ\text{C}$. The maximum amount of well-crystallized mullite was found in fly ash treated with 5% w/w MgO.

ACKNOWLEDGEMENTS

We are grateful to UGC (University Grants Commission) Government of India and DST (Department of Science & Technology), Government of India, for financial assistance.

REFERENCES

- [1] Y.M. Al-Jarsha, H .G. Emblem, K. Jones, A. M. D. Rahman, F .J. Davies, R. Wakefield and G.K. Sargent // *J. Mater. Sci.* **25** (1990) 2873.
- [2] H. Schneider, J. Schreuer and B. Hildmann // *J. Eur. Ceram. Soc.* **28** (2008) 329.
- [3] I. A. Aksay, D .M. Dabbs and M. Sarikaya // *J. Am. Ceram. Soc.* **74**(10) (1991) 2343.
- [4] A .K. Chakraborty // *J. Am. Ceram. Soc.* **74** (1991) 1401.
- [5] M. Belloto, A. Gualtieri, G. Artioli and S .M. Clark // *Phys. Chem. Miner.* **22** (1995) 207.
- [6] H. Schneider, K. Okada and J. Pask, In: *Mullite and Mullite Ceramics*, ed. by K. Okada (Wiley, Chichester, 1994), p. 4.
- [7] O .E. Manz // *Fuel* **76** (1997) 691.
- [8] I. Queralt, X. Querol, A. Lopez-Soler and F. Plana // *Fuel* **76** (1997) 787.
- [9] J .S. Jung, H .C. Park and R. Stevens // *J Mater Sci. Letts.* **20** (2001) 1089.
- [10] A. Olgun, Y. Erdog˘an, Y. Ayhan and B. Zeybek // *Ceram Inter.* **31** (2005) 153.
- [11] N. Chandra, N. Agnihotri, S. Bhasin and A .F. Khan // *J Euro Ceram Soc.* **25** (2005) 81.
- [12] K. Dana, S. Das and S .K. Das // *J Euro Ceram Soc.* **24** (2004) 3169.
- [13] L .F. Vilches, C. Fernandez-Pereira, J. Olivars del Valle and J. Vale // *Chem Eng J.* **95** (2003) 155.
- [14] X. Lingling, G. Wei, W. Tao and Y. Nanru // *Constr Build Mater.* **19** (2005) 243.
- [15] A. Jonker and J .H. Potgieter // *J Euro Ceram Soc.* **25** (2005) 3145.
- [16] Y. Fang, Y. Chen, M.R. Silsbee and D.M. Roy // *Materials Letters* **27** (1996) 155.

- [17] M. Criado, A. Fernandez-Jimenez and A. Palomo // *Microporous and Mesoporous Materials* **106** (2007) 180.
- [18] M .K. Haldar // *Ceramic International* **29** (2003) 573.
- [19] L .B. Kong, Y .Z. Chen, T .S. Zhang, J. Ma, F. Boey and H. Huang // *Ceramic International* **30** (2004) 1319.
- [20] L .B. Kong, T .S. Zhang, J. Ma and F. Boey // *Journal of Alloys and Compounds* **359** (2003) 292.
- [21] L .B. Kong, T .S. Zhang, J. Ma, F. Boey and R .F. Zhang // *Journal of Alloys and Compounds* **372** (2004) 290.
- [22] V. Viswabaskaran, F .D. Gnanam and M. Balasubramanian // *Appl. Clay Sci.* **25** (2004) 29.
- [23] R .L. Ore'fice and W .L. Vasconcelos // *J. Sol–Gel Sci. Technol.* **9** (1997) 239.