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Effect of barium to aluminium ratio on phases leading to barium aluminates

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Abstract

In our earlier studies, pure barium mono-aluminate and β_1 β_2-barium hexa-aluminate were prepared by keeping Ba/Al ratio as 1:2 and 1:12, respectively. In the present work, effect of varying Ba/Al ratio from 1:4 to 1:10 on the formation of barium aluminates has been studied. The samples obtained during hydrothermal precipitation contained mixtures of $BaCO_3$ and γ-AlOOH. The MCD (mean crystallite diameter) values along (1 1 1) plane corresponding to $BaCO_3$ phase for these precursors were in the range of 70–99 nm whereas the MCD values along (0 2 0) plane corresponding to γ-AlOOH were in the range of 10–12 nm. The precursors, when calcined at 400 °C did not show any crystalline phases of alumina and most of the peaks corresponded to barium carbonate with diminished peaks of γ-AlOOH when compared to the precursor. At 800 °C, some peaks for $(Al_2O_3)\underline{O}$ were observed along with major phase of $BaCO_3$. At 1200 °C, irrespective of the Ba/Al ratio, formation of major phase of $BaAl_2O_4$ along with minor phases of α-Al_2O_3 and Ba-β_{11}-Al_2O_3 were observed. At 1400 °C also $BaAl_2O_4$ remained the major phase at all Ba/Al ratios with crystalline phase of α-Al_2O_3. Typical peaks corresponding to Ba-β_{11}-Al_2O_3 aluminate became more prominent when the Ba/Al ratio was $\geq$1:6. No other intermediate phases such as tri-barium mono-aluminate, barium tetra aluminate or non-stoichiometric barium aluminates were formed.

Keywords: Hydrothermal; Calcination routes; Barium aluminates; XRD; Urea

1. Introduction

The barium aluminates are most widely used group of aluminates starting from industrial catalysts to structural ceramics in high temperature regions due to their superior physical properties. Several types of stoichiometric as well as non-stoichiometric aluminates are known. The most studied and also used aluminates of barium are the stoichiometric aluminates, such as: $BaO{\cdot}Al_2O_3$ (barium mono-aluminate), $3BaO{\cdot}Al_2O_3$ (tri-barium mono-aluminate), $BaO{\cdot}4Al_2O_3$ (barium tetra-aluminate) and $BaO{\cdot}6Al_2O_3$ (barium hexa-aluminate) [1–4]. The formation of each pure phase depends upon the preparation route and experimental conditions. Urea has been extensively used for precipitation of sub-micron and nano-sized oxide powders [5–9]. By using urea during hydrothermal precipitation and on calcining the precursors to as high temperature as 1200–1400 °C, the fine particle size may be retained. In our earlier work [10] micron-sized high surface area ceramic powders of barium hexa-aluminate having Ba-β-Alumina type structure were prepared through a hydrothermal precipitation–calcination route with the Ba/Al ratio as 1:12 and urea as the precipitating agent. Similarly, barium mono-aluminates [11] were synthesized by taking stoichiometric reaction mixture. Synthesis of high surface area Mn-doped barium hexa-aluminate was also reported [12]. In view of the above advantage of using urea as a precipitating agent, the present study involving investigation on the phase formation of barium aluminates by varying Ba/Al ratio in the range of 1:4 to 1:10 has been taken up.

2. Experimental

The chemicals used in the present investigation for the preparation of barium aluminates were of reagent grade (BDH India Ltd. or E-MERCK, India Ltd.). For a particular composition of barium aluminate, the required amount of stock solutions of barium nitrate (0.1 M) and aluminum nitrate

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Table 1
Code numbers for various samples

Hydrothermally prepared samples	
Ba:Al 1:4	S1
Ba:Al 1:6	S2
Ba:Al 1:8	S3
Ba:Al 1:10	S4
Calcined at 400 °C for 2 h	$S1^{400}$, $S2^{400}$, $S3^{400}$, $S4^{400}$
Calcined at 800 °C for 2 h	$S1^{800}$, $S2^{800}$, $S3^{800}$, $S4^{800}$
Calcined at 1200 °C for 2 h	$S1^{1200}$, $S2^{1200}$, $S3^{1200}$, $S4^{1200}$
Calcined at 1400 °C for 2 h	$S1^{1400}$, $S2^{1400}$, $S3^{1400}$, $S4^{1400}$

(1.0 M) were mixed thoroughly. To this mixed solution, urea was added (to get a urea/metal ratio of 2:1) and a complete homogeneous solution was made. The contents were then transferred into a 2 L capacity reactor (PARR Model 4542) for hydrothermal precipitation at 180 °C for 1 h. The contents were cooled to room temperature, washed to remove nitrates or any other soluble impurities [13], and dried in an air-oven at 110 °C. The dried samples were then calcined under static air conditions inside a muffle furnace at different temperatures, viz., 400, 800, 1200 and 1400 °C for 2 h. The conditions for hydrothermal precipitation and calcination were chosen based on our earlier studies [10,11]. The XRD patterns of the powder samples were recorded at a rate of 2°/min using a Philips PW 3710 X-Ray diffractometer (Cu target with Ni filter).

For convenience, the samples have been coded as given in Table 1.

3. Results and discussions

3.1. Probable reactions

In our earlier work [10], it was observed that during hydrothermal treatment the following reactions take place.

During hydrothermal precipitation at 180 °C:

(i) Hydrolysis of urea at 180 °C

$$NH_2{-}CO{-}NH_2 + H_2O \rightarrow 2NH_4OH + CO_2\,(g) \tag{1}$$

(ii) Reaction with barium nitrate

$$Ba(NO_3)_2 + CO_2\,(g) + H_2O \rightarrow BaCO_3\,(c) + 2HNO_3 \tag{2}$$

$$2HNO_3 + 2NH_4OH \rightarrow 2NH_4NO_3 + 2H_2O \tag{3}$$

with the overall reaction of formation of $BaCO_3$ as:

$$Ba(NO_3)_2 + NH_2{-}CO{-}NH_2 + H_2O \rightarrow BaCO_3\,(c) + 2NH_4NO_3 \tag{4}$$

(iii) Formation of boehmite

$$2Al(NO_3)_3 + 7NH_2{-}CO{-}NH_2 + 15H_2O \rightarrow 2AlOOH\,(c) + 6NH_4NO_3 + 4(NH_4)_2CO_3 + 3CO_2\,(g) \tag{5}$$

Calcination:

(i) On calcining at ∼400–800 °C

$$\underset{(boehmite)}{2AlOOH\,(c)} \underset{(-H_2O)}{\longrightarrow} Al_2O_3\,(ams.s) \tag{6}$$

(ii) On calcination at 1200–1400 °C

$$BaCO_3\,(c) + Al_2O_3\,(amp.s) \rightarrow BaAl_2O_4\,(c) + CO_2\,(g) \tag{7}$$

In the presence of excess alumina

$$BaCO_3\,(c) + 2Al_2O_3\,(amp.s) \rightarrow BaO \cdot 2Al_2O_3\,(c) + CO_2\,(g) \tag{8}$$

$$BaCO_3\,(c) + 3Al_2O_3\,(amp.s) \rightarrow BaO \cdot 3Al_2O_3\,(c) + CO_2\,(g) \tag{9}$$

$$BaCO_3\,(c) + 4Al_2O_3\,(amp.s) \rightarrow BaO \cdot 4Al_2O_3\,(c) + CO_2\,(g) \tag{10}$$

$$BaCO_3\,(c) + 5Al_2O_3\,(amp.s) \rightarrow BaO \cdot 5Al_2O_3\,(c) + CO_2\,(g) \tag{11}$$

Considering the various other phases such as tri-barium mono-aluminate or a combination of aluminates, the following reactions may also take place:

$$3BaCO_3\,(c) + 6Al_2O_3\,(amp.s) \rightarrow BaO \cdot 6Al_2O_3\,(c) + 2BaO\,(c) + 3CO_2\,(g) \tag{12}$$

$$BaCO_3\,(c) + 2Al_2O_3\,(amp.s) \rightarrow BaO \cdot Al_2O_3\,(c) + Al_2O_3\,(c) + CO_2\,(g) \tag{13}$$

$$3BaCO_3\,(c) + 6Al_2O_3\,(amp.s) \rightarrow 3BaO \cdot Al_2O_3 + 3Al_2O_3\,(c) + 3CO_2\,(g) \tag{14}$$

(amp.: amorphous, s: solid, c: crystalline or polycrystalline, g: gaseous all other are aqueous species).

3.2. XRD studies

3.2.1. XRD analysis of hydrothermally prepared precursors at 180 °C

The XRD patterns of the four samples namely S1, S2, S3 and S4 prepared at 180 °C are given in Fig. 1. Most of the peaks are characteristic of crystalline $BaCO_3$ [14a]. Four identifiable peaks at $2\theta \sim 16°$–$17°$, 44.3°, 52° and 57° confirm the presence of crystallites of boehmite [14b]. MCD values calculated by taking into consideration the major planes for barium carbonate [(1 1 1) plane, *d*-value ∼3.73 Å] and boehmite [(0 2 0) plane, ∼*d*-value 6.14 Å] are shown in Fig. 2. It is observed that the barium carbonate crystallites size increase from 70.9 to 99.3 nm by increasing the Ba/Al ratio from 1:4 to 1:6 and thereafter remains constant. The crystallite size of boehmite was found to be almost 1/7th to 1/9th the size of barium carbonate in the studied range of Ba/Al ratio.

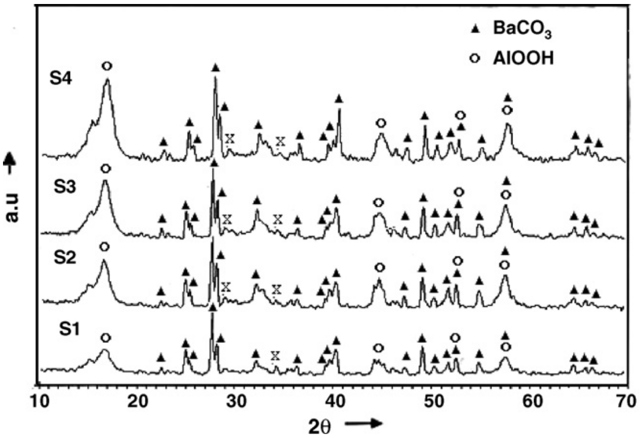

Fig. 1. XRD pattern of hydrothermally prepared precursor samples S1, S2, S3 and S4.

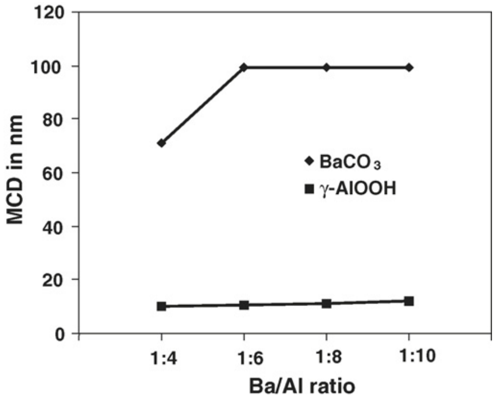

Fig. 2. Effect of Ba/Al ratio on the MCD values of major planes of $BaCO_3$ and γ-AlOOH.

3.2.2. XRD studies of samples calcined at 400–1400 °C

The precursor samples S1, S2, S3 and S4 were calcined at 400, 800, 1200 and 1400 °C and the X-ray diffraction patterns of all the sixteen samples were taken. The crystalline phases observed in these samples along with relative intensities of specific major peaks corresponding to these crystalline phases are given in Table 2. Similar to the precursor samples, the only crystalline phases obtained at 400 °C calcination temperature were of boehmite (γ-AlOOH) and barium carbonate. The peak intensities at *d*-values = 6.11 Å corresponding to γ-AlOOH were found to decrease at 400 °C as compared to their respective precursor samples except for sample S1. There was no such trend for barium carbonate peaks. Diminishing of boehmite peaks may be due to partial conversion to amorphous aluminum oxide.

The XRD patterns of the samples heated at 800 °C showed that the major crystalline phase still correspond to barium carbonate. Formation of $(Al_2O_3)\underline{O}$ [14c] (sys-*ortho*-rhombic aluminum oxide) was observed in all the samples. Formation of such phase of aluminum oxide has not been reported in any earlier work. Usually, the phase formed is either γ-Al_2O_3 or aluminum oxide remains in the amorphous form. The XRD patterns also show distinct reflections for barium mono-aluminate ($BaAl_2O_4$) at *d*-values of 3.16 Å [14d] indicating the start of formation of the barium mono-aluminate phase around this temperature from the interim forms of barium carbonate and aluminum oxide/oxy-hydroxide. It is quite interesting to note that with the increase in Ba/Al ratio from 1:4 to 1:10, the relative intensity of barium mono-aluminate peak decreased.

The XRD patterns of samples calcined at 1200 °C coded as S1^{1200}, S2^{1200} S3^{1200} and S4^{1200} showed that irrespective of Ba/Al ratio, barium mono-aluminate ($BaAl_2O_4$) [14d] is the major phase (Table 2). In all the patterns peaks with 100% R.I. at *d*-value of ~3.14 Å correspond to $BaAl_2O_4$. However, the peak intensity decreases with the increase in Ba/Al ratio. Formation

Table 2
Relative intensities of major crystalline phases obtained from XRD patterns of precursors calcined at different temperatures

Sample code	γ-AlOOH % R.I. of peak at *d*-value 6.14 Å	$BaCO_3$ % R.I. of peak at *d*-value 3.72 Å	$(Al_2O_3)\underline{O}$ % R.I. of peak at *d*-value 2.79 Å	α-Al_2O_3 % R.I. of peak at *d*-value 3.47 Å	$BaAl_2O_4$ % R.I. of peak at *d*-value 3.16 Å	Ba-β_{11}-Al_2O_3 % R.I. of peak at *d*-value 2.71 Å
S1^{400}	34.7	100				
S2^{400}	31.1	100				
S3^{400}	21.1	100				
S4^{400}	20.0	100				
S1^{800}		100	7.6		26.0	
S2^{800}		100	12.6		17.9	
S3^{800}		100	16.2		13.9	
S4^{800}		100	17.2		10.9	
S1^{1200}				30.3	100	
S2^{1200}				32.7	100	2.2
S3^{1200}				34.0	100	4.4
S4^{1200}				34.9	100	7.5
S1^{1400}				27.7	100	
S2^{1400}				32.1	100	15.4
S3^{1400}				32.2	100	16.0
S4^{1400}				40.2	100	53.5

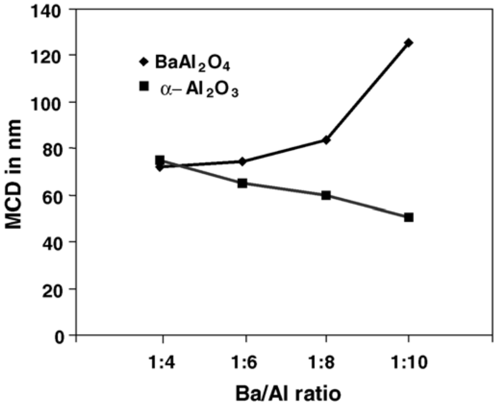

Fig. 3. Effect of Ba/Al ratio on the MCD of major planes of $BaAl_2O_4$ and α-Al_2O_3 formed at 1200 °C.

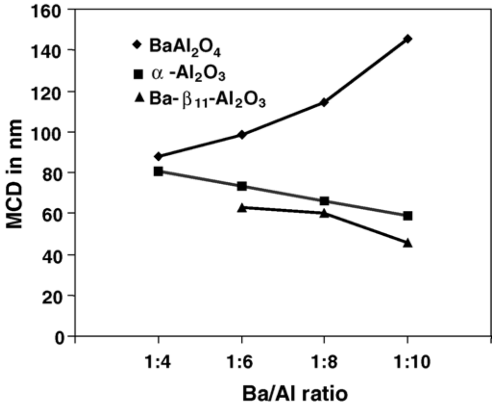

Fig. 5. Effect of Ba/Al ratio on the MCD of major planes of $BaAl_2O_4$, Ba-$β_{11}$-Al_2O_3 and α-Al_2O_3 formed at 1400 °C.

of tri-barium mono-aluminate as an intermediate has been reported in many studies [1–4,15,16] whereas in our earlier study [10] as well as in the present study, barium mono-aluminate is formed without formation of any other reported intermediate aluminate. With the increase of Ba/Al ratio, formation of Ba-β-Al_2O_3 [14e] type hexa-aluminate was observed. α-Al_2O_3 was present in all the samples. Effect of Ba/Al ratio on MCD values along the major plane of two compounds, i.e., $BaAl_2O_4$ [(2 0 2) plane, *d*-value ~3.16 Å and α-Al_2O_3 [(0 1 2) plane, *d*-value 3.47 Å] are shown in Fig. 3. It is observed that the MCD values for barium aluminate increase from 71.8 to 125.7 nm whereas the MCD values for α-Al_2O_3 decrease from 71 to 50.4 nm with the increase in Ba/Al ratio from 1:4 to 1:10. MCD values for hexa-aluminate were not calculated as it was present as minor phase.

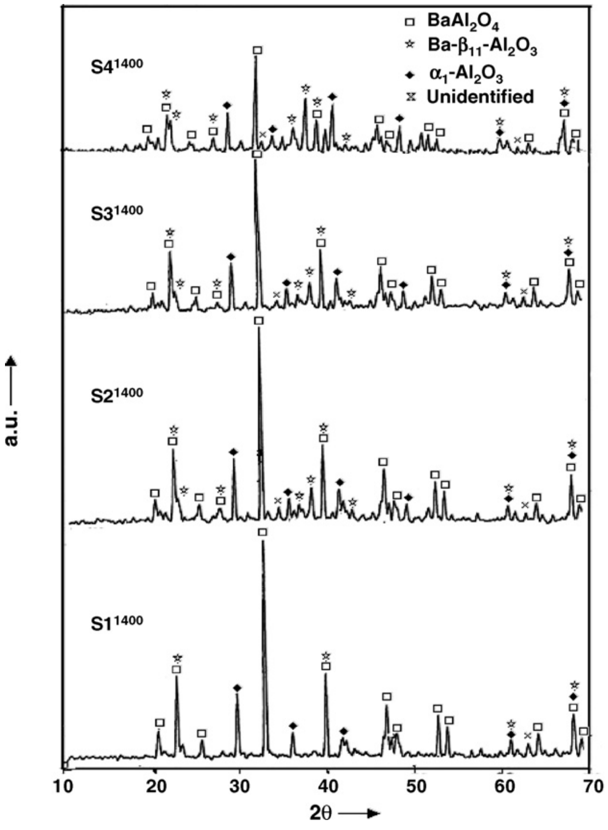

Fig. 4. XRD patterns of the samples heated at 1400 °C.

XRD patterns of samples $S1^{1400}$, $S2^{1400}$ $S3^{1400}$ and $S4^{1400}$ show crystalline phases of $BaAl_2O_4$ [14d], Ba-$β_{11}$-Al_2O_3 and α-Al_2O_3 (Fig. 4). However, the crystallinity of both Ba-$β_{11}$-Al_2O_3 and α-Al_2O_3 phases increase as evident by typical peaks of Ba-$β_{11}$-Al_2O_3 at *d*-values of ~4.48, 2.79, 2.69, 2.51 Å and typical peaks of α-Al_2O_3 at ~3.47, 2.55, 2.13 Å. In many earlier studies on preparation of barium aluminates formation of various alumina phases such as θ-Al_2O_3, δ-Al_2O_3 and γ-Al_2O_3 have been reported at 1200–1400 °C [17,18], while in this study only α-Al_2O_3 phase is formed. Effect of Ba/Al ratio on MCD values along the major plane of three compounds, i.e., $BaAl_2O_4$ [(2 0 2) plane, *d*-value ~3.16 Å], Ba-$β_{11}$-Al_2O_3 (*d*-value ~4.48 Å) and α-Al_2O_3 [(0 1 2) plane, *d*-value 3.47 Å] are shown in Fig. 5. As observed at 1200 °C, MCD values for mono-aluminate increases and those of α-Al_2O_3 decrease with the increase of Ba/Al ratio. The MCD values for Ba-$β_{11}$-Al_2O_3 decrease from 62.7 to 45.38 nm with the increase of Ba/Al ratio from 1:6 to 1:10. The larger values of MCD for barium mono-aluminate could be due to 1:2 molar ratio of Ba/Al wherein the individual size of precursor $BaCO_3$ with 70–99 nm is much larger as compared to that of γ-AlOOH (10–12 nm). In case of barium hexa-aluminate, molar ratio of Ba/Al increases to 1:12 and the smaller size of aluminum precursor predominates in the formation of hexa-aluminate resulting in reduction in the crystallite size.

4. Conclusions

Hydrothermally prepared precursors at 180 °C taking Ba/Al ratios as 1.4, 1:6, 1:8 and 1:10 showed presence of crystalline barium carbonate and boehmite. These precursors when calcined to 400 °C retained the same crystalline phases though the relative intensities varied. When the calcination temperature was increased to 800 °C, barium carbonate remained the major phase with appearance of $(Al_2O_3)\underline{O}$ phase of aluminum oxide. $BaAl_2O_4$ starts forming at 800 °C as a few peaks corresponding to this compound were identified. Calcination of precursors at about 1200 °C resulted in the formation of barium mono-aluminate as the major phase at all Ba/Al ratios with formation of α-Al_2O_3 as minor phase. Sample having Ba/Al ratio 1:4, calcined at 1400 °C showed the presence of $BaAl_2O_4$ as the major phase where as samples having Ba/Al ratio $\geq$1:6 contained $BaAl_2O_4$ along with distinct peaks of Ba-β_{11}-Al_2O_3 and α-Al_2O_3. The MCD values estimated from the major peaks of barium mono-aluminate increased whereas those of Ba-β_{11}-Al_2O_3 and α-Al_2O_3 decreased with the increase of Ba/Al ratio. In the entire studied range of Ba/Al ratio (1:4 to 1:10), barium mono-aluminate and/or hexa-aluminate with minor amounts of α-Al_2O_3 were obtained.

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References

[1] M.I. Zaki, G.A.M. Hussien, R.B. Fahim, Characterisation of the powder mixture of the reaction between alumina and barium carbonate, J. Mater. Sci. Lett. 4 (1985) 517–522.

[2] L. Perier-Camby, A.M. Vernay, G. Thomas, Solid way synthesis of barium aluminate. High temperature X-ray diffraction study of intermediary compounds, Mater. Sci. Forum 79-82 (1991) 671–680 (EPDIC 1, Pt.2).

[3] L. Perier-Camby, G. Thomas, Chemical reaction for preparation of $BaAl_2O_4$; study of reaction kinetics and mechanism, J. Chim. Phys. Chim. Biol. 91 (11/12) (1994) 1763–1773.

[4] I.W.H. Gitzen, Alumina as a ceramic material, Am. Ceram. Soc. Columbus, Ohio (1970) 141.

[5] T. Herńandez, C. Bautista, P. Mart'ýn, Synthesis and thermal evolution of Mn-doped alumina nanoparticles by homogeneous precipitation with urea, Mater. Chem. Phys. 92 (2005) 366–372.

[6] S.R. Dhagea, R. Pasrichab, V. Ravia, Preparation of ferroelectric $BaNb_2O_6$ by the urea method, Mater. Lett. 59 (2005) 1929–1931.

[7] F. Boschini, B. Robertz, A. Rulmont, R. Cloots, Preparation of nanosized barium zirconate powder by thermal decomposition of urea in an aqueous solution containing barium and zirconium, and by calcination of the precipitate, J. Eur. Ceram. Soc. 23 (2003) 3035–3042.

[8] J. Subrt, J. Bohác¢ek, V. Tengl, T.'s¢ Grygar, P. Bezdic¢ka, Uniform particles with a large surface area formed by hydrolysis of $Fe_2(SO_4)_3$ with urea, Mater. Res. Bull. 34 (1999) 905–914.

[9] M. Akinc, N. Jougen, J. Lemattre, H. Hofmann, Synthesis of nickel hydroxide powders by urea decomposition, J. Eur. Ceram. Soc. 18 (1998) 1559–1564.

[10] D. Mishra, S. Anand, R.K. Panda, R.P. Das, Preparation of barium hexa-aluminate through a hydrothermal precipitation–calcination route and characterization of intermediate and final products, Mater. Lett. 56 (2002) 873–879.

[11] D. Mishra, S. Anand, R.K. Panda, R.P. Das, Characterization of products obtained during formation of barium monoaluminate through hydrothermal precipitation–calcination route, J. Am. Ceram. Soc. 85 (2002) 437–443.

[12] D. Mishra, S. Anand, R.K. Panda, R.P. Das, Synthesis of high-surface area Mn-doped barium hexa-aluminates by a combination of hydrothermal precipitation–calcination route, Mater. Chem. Phys. 82 (2003) 892–896.

[13] A.I. Vogel, A Text Book of Quantitative Inorganic Analysis, fifth ed., The English Language Book Society and Longmans Green and Co, 1998.

[14] Joint Committee On Powder Diffraction Standard (JCPDS), International Center For Diffraction Data, Swathmore, PA, File Nos. (a) 5-378, (b) 21-1307, (c) 16-435, (d) 17-306 and (e) 30-143, 1994.

[15] M.M. Alli, S.K. Agarwal, S. Agarwal, S.K. Handoo, Kinetics and diffusion studies in $BaAl_2O_4$ formation, Cem. Concr. Res. 25 (1995) 86–90.

[16] T.J. Davies, W.A. Al-Douri, M. Biedermann, Q.G. Chen, H.G. Emblem, Refractory oxides containing barium, J. Mater. Sci. Lett. 15 (6) (1996) 482–487.

[17] W.J. Dawson, Hydrothermal synthesis of advanced ceramic powders, J. Am. Ceram. Soc. Bull. 67 (10) (1988) 1673–1678.

[18] T. Assih, A. Ayral, M. Abenoza, J. Phalippou, Raman study of alumina gels, J. Mater. Sci. 23 (1988) 3326–3331.