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HYDRATION REACTIONS OF NONSTOICHIOMETRIC BARIUM ORTHOALUMINATES

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ABSTRACT

The hydration reactions of the nonstoichiometric barium orthoaluminates having the chemical formula $Ba_{1-x}Al_2O_{4-x}$ ($0<x<0.56$) are studied. On exposure to CO_2-free humid air, this compound reacted to form a new hydration product, barium alumino hydroxy hydrate, $Ba_{1-x}Al_2(OH)_{8-2x}\cdot yH_2O$, wherein Al^{3+} is in octahedral coordination, as indicated by ^{27}Al magic angle spinning nuclear magnetic resonance (MAS NMR). The formation of hydrated product is faster for the nonstoichiometric compositions ($x > 0$). The collapse of the nepheline-type structure of barium orthoaluminate is explained in terms of the relative migration of Ba^{2+} ions from the structural channels. Increases in the reaction rate for the nonstoichiometric samples are attributed to faster diffusion of the hydroxyl ions in the lattice, assisted by the structural vacancies. The product is highly sensitive to CO_2; on exposure this compound gives rise to barium aluminium carbonato-oxy-hydroxide and eventually segregates to $BaCO_3$ and aluminium hydroxide. On heating the hydrated product to 600°C, the compound decomposed to $Ba_{1-x}Al_2O_{4-x}$, indicating the reversibility of the reaction. The reactions involved, microstructural changes, and the possible mechanism of formation of hydrated products are discussed in detail. © *1998 Elsevier Science Ltd*

Introduction

Barium orthoaluminate and its hydrates are used in formulating refractory concretes (1–3) and radiation proof plasters (4,5). These compounds have good absorption capability of X-rays and gamma rays and, hence they are suitable for radiation proof shielding concretes. When doped with Eu^{2+}, barium orthoaluminate is useful in fluorescent lamp phosphor blends as a green emitter (6), although less efficient than hexa-aluminates. Recently, we reported (7) a large range of nonstoichiometry in barium orthoaluminate corresponding to the chemical formula $Ba_{1-x}Al_2O_{4-x}$ with $0<x<0.56$, when prepared through the chemical method of gel to crystallite conversion (G-C). Barium orthoaluminate belongs to the nepheline-type structure which consists of corner shared AlO_4 framework and the structural channels are occupied by Ba^{2+} ions. Nepheline (8) is a stoichiometric member of the "stuffed" tridymite family (8). Tridymite (8) in turn, is a polymorphic form of silica which has framework of

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corner shared SiO_4 tetrahedra arranged in six-fold rings with adjacent tetrahedra directed in opposite directions forming a one-dimensional sheet. The sheets are arranged in the -AB-AB- pattern forming hexagonal close packing. In this structure there are large open channels in the framework and these provide suitable sites for additional cations, provided the charge on the framework is reduced by replacing Si^{4+} atoms by Al^{3+} atoms. This type of structure has been called a "stuffed" tridymite, wherein the structural channels are partially filled. The observed large deviation from stoichiometry of barium orthoaluminate is explained in terms of the variable occupancy of Ba^{2+} ions in the channels and the associated oxygen vacancies within the corner sharing AlO_4 network. The coordination of Al^{3+} remained tetrahedral in the whole range of nonstoichiometry as characterised using solid-state magic angle spinning nuclear magnetic resonance (MAS NMR). Nonstoichiometric samples showed higher degree of disorder in comparison to that of the stoichiometric composition. The present paper deals with the hydration reaction of these samples on exposure to humid ambients. The samples reacted slowly with water vapour and degraded completely into different products.

Experimental

The samples of barium orthoaluminate were prepared through gel to crystallite conversion technique as presented in our previous publications (7,9,10). Air dried samples were preheated at 1400°C to ensure that there were no residual hydroxyl ions. The samples were then exposed to humid atmosphere in a pre-evacuated glove box and then filled with synthetic air (mixture of $N_2 + O_2$ of 80:20 by volume), wherein the entry of CO_2 was prevented by alkali (Ascarite) guard-tubes. For the electrical resistivity and micrographic studies, sintered pellets of the same compositions were exposed to humid atmosphere. Hydration reaction products were characterised by X-ray diffraction (XRD) patterns of the samples exposed for different time intervals, using Scintag (USA) X-ray diffractometer. Thermal analyses were performed on a simultaneous thermogravimetry–differential thermal analysis (TG/DTA) instrument from Polymer Laboratory STA–1500(UK) at a heating rate of 5°C/min. Infrared absorption spectra was recorded on a Perkin Elmer (USA) spectrometer in the range 4000–250 cm^{-1}. Solid state ^{27}Al MAS NMR spectra were obtained at 78.2 MHz using a high resolution NMR spectrometer (BRUKER 300 MHz) at room temperature fitted with a Magic Angle Spinning probe (MAS) for rotating the sample at a frequency of 7 kHz. ^{27}Al MAS NMR chemical shifts (δ) were referenced to 1 M $Al(H_2O)_6Cl_3$ solution having the assigned $\delta = 0$. The microstructural analyses were carried out using S360 Cambridge scanning electron microscope. The electron gun was operated at an energy of 20kV with a beam diameter of 200–250 Å. Elemental distribution analysis on the specimens was performed by a fully automated quantitative Energy Dispersive X-ray analyser (EDX) fitted on to this microscope. Electrical resistance measurements were carried out using a Hewlett-Packard high resistance meter, model HP4339A.

Results

Samples reacted slowly on exposure to humid atmosphere, forming a gel-like mass over a time interval of 24 h. The period it took for the formation of the gel depended upon the relative humidity (RH). The reaction is faster under 100% RH conditions. If the uncombined water is removed slowly after the hydration by evacuating, using a rotary pump or by

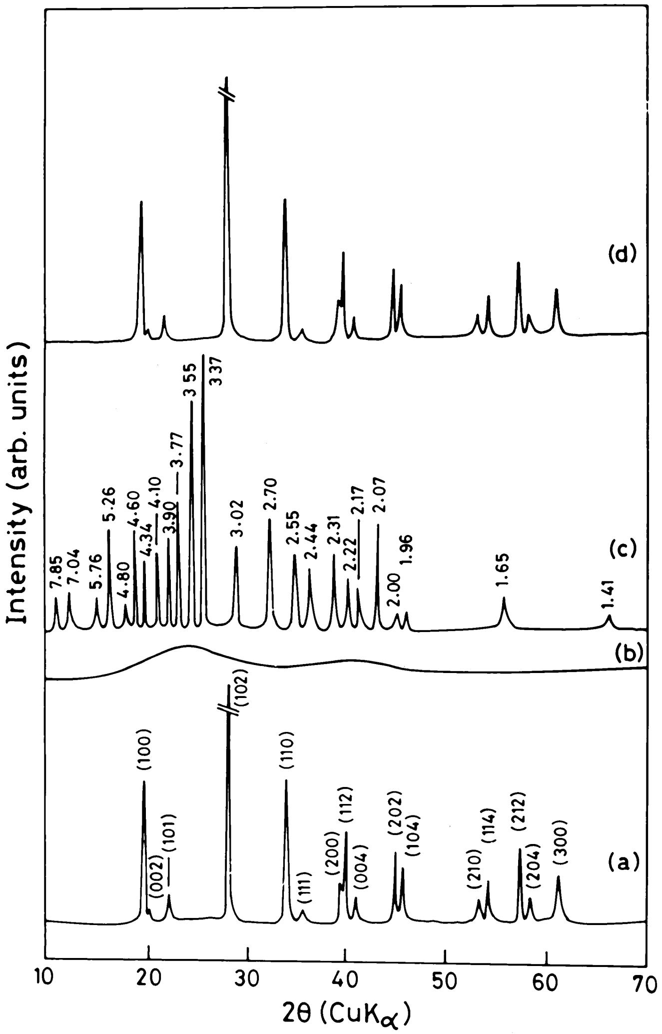

FIG. 1.

XRD patterns of $Ba_{0.76}Al_2O_{3.76}$ (*a*) unexposed; after exposing to humid atmosphere for (*b*) 4 h, (*c*) 48 h; (*d*) is the XRD pattern obtained after heating the hydrated product to 600°C.

decreasing the RH to $\leq$ 50%, the gel sets permanently as a hard mass. On the other hand, the gel-like mass slowly swells on continuous exposure to moisture (RH $\geq$ 90%) for 38 to 60 h, depending upon the *x*-value. The time taken by the nonstoichiometric end-member $Ba_{0.44}Al_2O_{3.44}$ to convert into hydrated product is only 38 h, whereas for stoichiometric $BaAl_2O_4$, the time taken was above 60h. X-ray diffraction (XRD) patterns of one of the samples, viz., $Ba_{0.76}Al_2O_{3.76}$, exposed to humid air of RH $>$ 90% for various intervals of time are shown in Figure 1. The gel-like mass formed after 2 to 3 h of exposure is completely amorphous to X-rays (Fig. 1b), wherein all the X-ray reflections of barium orthoaluminate

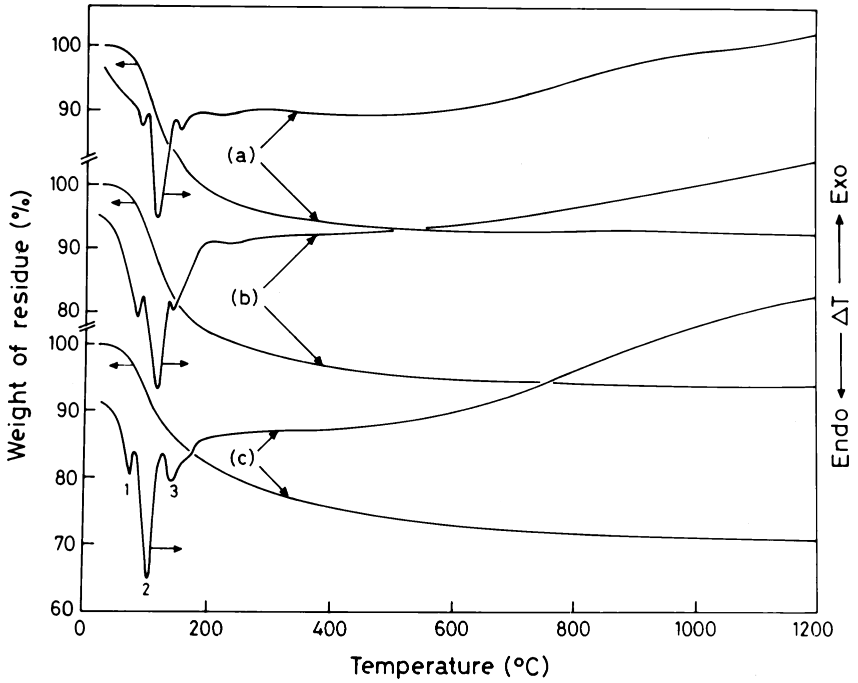

FIG. 2.

TG/DTA plots of (*a*) $BaAl_2(OH)_8\cdot\frac{1}{2}H_2O$ (*b*) $Ba_{0.76}Al_2(OH)_{7.52}\cdot H_2O$, and (*c*) $Ba_{0.44}Al_2(OH)_{6.88}\cdot 1.5\ H_2O$. The peaks marked 1, 2, 3 on the DTA curve indicates the endothermic peaks due to the loss of adsorbed water (*1*), loss of hydroxyl groups associated with Al^{3+} (*2*), and oxygen vacancy sites (*3*) respectively.

have vanished. The gel-like mass started swelling after exposure > 28 h. At this stage, a new XRD pattern (Fig. 1c) was observed that could not be indexed on the basis of the reported data of barium hydroxide nor of the barium aluminate hydrates reported by Ahmed and Glasser (1). The resultant phase is a barium aluminium hydroxy hydrate, $Ba_{1-x}Al_2(OH)_{8-2x}\cdot yH_2O$ ($0 < x < 0.56$, $0.5 < y < 2$ H_2O), wherein Al is in 6-coordination rather than in 4-coordination as observed in the parent composition (Ba-orthoaluminate), which is further confirmed by the solid state ^{27}Al MAS NMR results presented subsequently in this paper. The other samples ($x=0$ and 0.56) showed a similar XRD pattern. On heating the hydrated sample to 600°C, the product formed was single phasic barium orthoaluminate, indicating the complete reversibility of the reaction.

Introduction of CO_2 into the reaction chamber resulted in the insertion of CO_2 into the sample as observed by the infrared absorption spectra, which shows the absorption due to the carbonato group. As the partial pressure of CO_2 in the reaction chamber is increased, the phase was no more barium alumino hydroxy hydrate. The extreme case is the formation of $BaCO_3$ as the major product along with aluminium hydroxide. Phase-pure hydration products can be obtained only on taking extreme care to avoid CO_2 by using a glove box and purging with high purity argon gas or synthetic air.

Thermal Analyses

The thermal characteristics (Fig. 2) of the Ba-aluminium hydroxy hydrate formed is completely different from that of the hydrated barium orthoaluminate phases reported by Ahmed and Glasser (1). All the hydrated samples (irrespective of the x-values), showed similar TG/DTA curves with total weight loss of ~ 30%. TGA indicates that the major weight loss is in the temperature range 30 to 400°C (25%). The weight loss (~6%) below 100°C is due to the loss of adsorbed water. Corresponding endotherm is observed in the DTA curve at 70°C. The weight loss (19%) in the range 100 to 400°C is due to the loss of hydroxyl groups associated with Al^{3+} and Ba^{2+}. The TGA curve shows a continuous weight loss without distinct steps corresponding to loss of hydroxyl groups associated with either Al^{3+} or Ba^{2+}. However, the DTA curve shows two distinct endothermic peaks around 102 and 140°C. The strong peak ~102°C is due to loss of hydroxyl groups associated with Al^{3+} whereas the 140°C peak is due to the loss of hydroxyl groups occupying the oxygen vacancy sites. The minor weight loss of 3–5% above 400°C up to 600°C is due to the loss of residual hydroxyl groups associated with Ba^{2+} having more ionicity. DTA curves of the nonstoichiometric compounds (Fig. 2 a-b) show shift in the second endothermic peak to 110°C. This indicates that the hydroxyl groups in the nonstoichiometric form are somewhat more strongly bound. X-ray analyses of the hydrated sample treated at 600°C showed barium orthoaluminate as the single phase.

Based on the thermal analyses results, the empirical formula that can be suggested is $Ba_{1-x}Al_2(OH)_{8-2x}{\cdot}yH_2O$ (where $0 < x < 0.56$ and $0.5 < y < 2$). The overall reactions can be represented as follows (Eqs. 1–7):

Hydroxylation

$$Ba_{1-x}Al_2O_{4-x}(0 < x < 0.56) + (4 - x)\,H_2O \xrightarrow{\text{100\% humidity}} Ba_{1-x}Al_2(OH)_{8-2x} \qquad (1)$$

Hydration

$$Ba_{1-x}Al_2(OH)_{8-2x} + yH_2O \xrightarrow[>60\text{ h}]{\text{100\% humidity}} Ba_{1-x}Al_2(OH)_{8-2x}{\cdot}yH_2O(0.5 < y < 2) \qquad (2)$$

In Presence of $H_2O + CO_2$

$$Ba_{1-x}Al_2O_{4-x} + yH_2O + zCO_2 \xrightarrow[\text{38–60 h}]{\text{100\% humidity}} \begin{matrix} Ba_{1-x}Al_2 \\ (0.5 < y < 2) \end{matrix}$$

$$\times\,(CO_3)_zO_w(OH)_{8-2(w+x+z)}{\cdot}yH_2O \qquad (3)$$

Heat Treatment of Hydrated Product

$$Ba_{1-x}Al_2(OH)_{8-2x}{\cdot}yH_2O \xrightarrow{<100°C} Ba_{1-x}Al_2(OH)_{8-2x} + yH_2O \qquad (4)$$

$$Ba_{1-x}Al_2(OH)_{8-2x} \xrightarrow{<150°C} Ba_{1-x}Al_2O_3(OH)_{2-x} + 3H_2O(\Delta w = 17\%) \qquad (5)$$

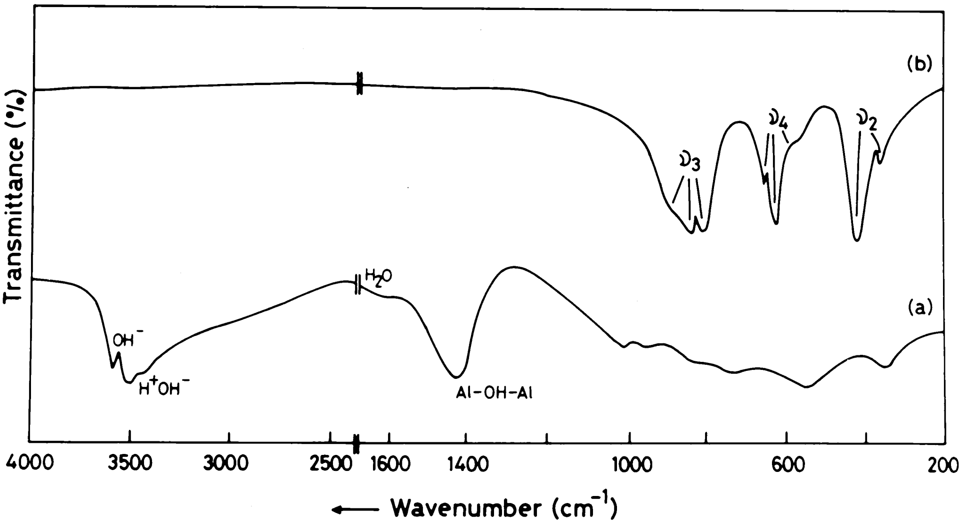

FIG. 3.

IR spectra of (*a*) $Ba_{0.76}Al_2(OH)_{7.52}{\cdot}H_2O$. (*b*) The spectrum obtained after heating the hydration reaction product to 600°C. The absorption bands of AlO_4 tetrahedra are indicated on curve (*b*). Bending (ν_2) shows two bands at 420 and 360 cm^{-1}. Asymmetric stretching (ν_3) and asymmetric bending (ν_4) show three absorption bands each (*b*).

$$Ba_{1-x}Al_2O_3(OH)_{2-x} \xrightarrow{<400°C} Ba_{1-x}Al_2O_{3.5-x}(OH) + \tfrac{1}{2}H_2O(\Delta w = 3\%) \tag{6}$$

$$Ba_{1-x}Al_2O_{3.5-x}(OH) \xrightarrow{600°C} Ba_{1-x}Al_2O_{4-x}(0 < x < 0.56) + \tfrac{1}{2}H_2O(\Delta w = 3\%) \tag{7}$$

Infrared Absorption Spectra

The presence of hydroxyl groups and water of hydration are further confirmed by infrared (IR) absorption spectra. Figure 3 shows the IR spectra of the hydrated samples in relation to that of barium orthoaluminate. Presence of the sharp absorption band at 3600 cm^{-1} is indicative of the absorption due to the ionic OH groups, and the shallow band centred at 3500cm^{-1} is due to the H-OH stretching of water. The band at 1630cm^{-1} is due to the bending vibrations of H_2O molecule. Absorption bands below 1200cm^{-1} are very broad and structureless; hence, the assignment is not possible. Absorption band at 1440 cm^{-1} is due to the vibrations of Al–OH–Al groups wherein each of the OH group is bridged to the neighbouring Al^{3+} ions. On heating the sample to 600°C the absorption spectrum corresponds to that of barium orthoaluminate, wherein the totally symmetric Al–O stretching frequency is absent. Degeneracy is lifted for the other modes of vibrations of AlO_4 tetrahedra so that symmetric bending (ν_2) shows two bands at 420 and 360 cm^{-1}. Asymmetric stretching (ν_3) and asymmetric bending (ν_4) show three absorption bands each (Fig. 3b).

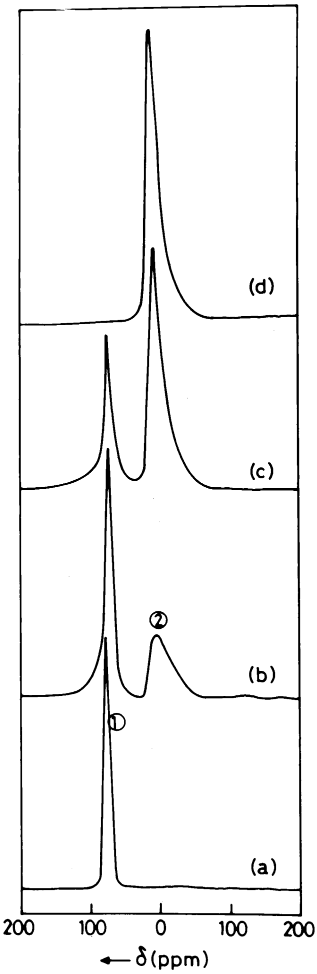

FIG. 4.

Solid state ^{27}Al MAS NMR of $Ba_{0.76}Al_2O_{3.76}$ as a function of time of exposure to humidity (*a*) before exposure, (*b*) exposed for 4 h, (*c*) exposed for 24 h, and (*d*) exposed for >48 h. The peaks marked 1 and 2 arise from the resonance behaviour of Al^{3+} in tetrahedral and octahedral coordination, respectively.

Solid State ^{27}Al MAS NMR Results

The change in the position of resonance absorption due to Al^{3+} ions as the hydration reaction proceeds, due to changing coordination in the resultant product, is shown in Figure 4 for the composition of $Ba_{0.76}Al_2O_{3.76}$ as a function of time of exposure to the humid atmosphere. In barium orthoaluminate, Al^{3+} has the tetrahedral coordination, and the resonance peak is observed at 71 ppm. The reported value of chemical shift is 69 ppm for $BaAl_2O_4$ (11), which represents the resonance behaviour of Al^{3+} in tetrahedral coordination. NMR spectra of the

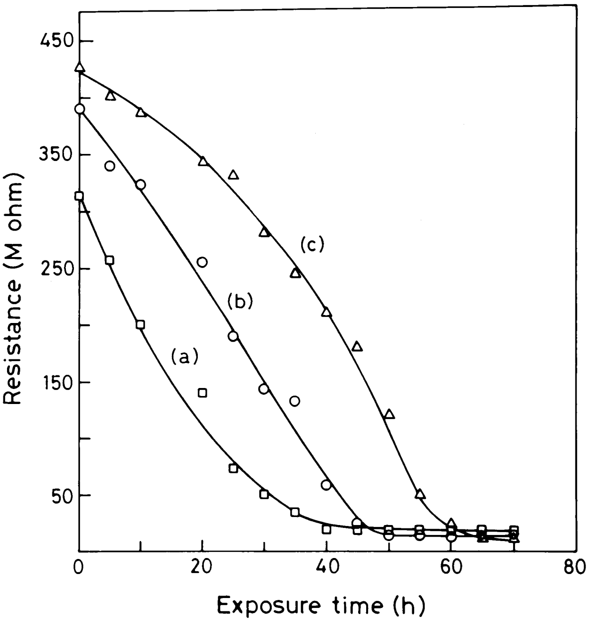

FIG. 5.
Variation of electrical resistance with time of exposure for the composition $Ba_{1-x}Al_2O_{4-x}$, (*a*) $x = 0.56$, (*b*) $x = 0.24$, (*c*) $x = 0$.

samples after exposure to moisture for 4 h show an additional resonance peak at $\delta = 5$ ppm, which is due to the resonance of Al^{3+} in the octahedral site. As the exposure time to moisture is increased, the intensity of the resonance peak due to Al^{3+} in the octahedral coordination increased (Fig. 4c) and that of the tetrahedral coordination decreased (Fig. 4b), indicating the continuous conversion of Ba-orthoaluminate into hydrated products wherein Al^{3+} has the octahedral coordination. Prolonged exposure (>48 h) to the humidity resulted in the complete change of the Al^{3+} coordination from tetrahedral to octahedral (Fig. 4d). With increase in the value of x, the time taken for the conversion of Al^{3+} coordination from tetrahedral to octahedral is decreased. For the stoichiometric composition ($x = 0$) the time taken was ~60h and for the extreme case of nonstoichiometry ($x = 0.56$) conversion time required is ~38h in agreement with the X-ray diffraction results. These results are further confirmed by the electrical resistance measurement, which varies with the extent of hydroxylation.

Electrical Measurements

Variation in the kinetics of hydration reaction can be conveniently followed by the electrical resistance measurements, as electrical resistance varies with the extent of hydroxylation of the sample. For the electrical resistance measurements, sintered pellets, gold-coated on both sides, were exposed to humidity in a glove box. Electrical measurements were carried out at different time intervals. Figure 5 shows variation of resistance as a function of exposure time for $Ba_{1-x}Al_2O_{4-x}$ for $x = 0$, 0.24 and 0.56. All the samples show saturation in electrical

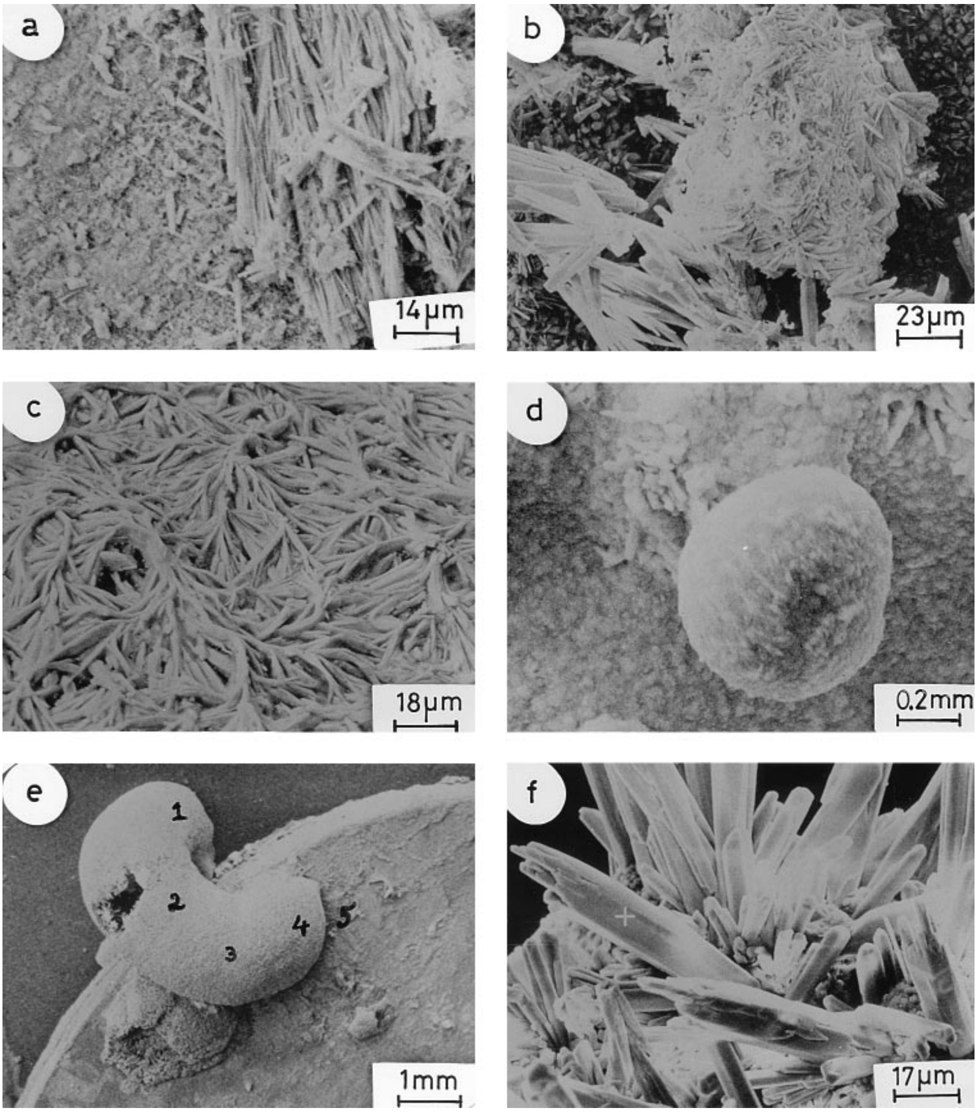

FIG. 6.
SEM micrograph of the sample at different time intervals of exposure to moist atmosphere for (*a*) 2 h, (*b*) 6 h, (*c*) 12 h. (*d*) Initial stage of the growth on the pellet after exposing $>$ 28 h to humid atmosphere. (*e*) Photograph of the outwardly grown hydrated product, positions marked (*1-5*) are the positions where the EDX analysis was taken. (*f*) Micrograph of the needular crystal projecting out from the pellet after removing the outwardly grown region.

conductivity above a certain exposure time. It is evident from the figure that hydration reaction is very slow in the case of stoichiometric composition, as indicated by the continuous fall in electrical resistance and attainment of a limiting value above 60 h, indicative of the completion of hydroxylation. The composition with $x = 0.56$ shows a drastic decrease in

TABLE 1
Results of EDX analysis at various positions marked in Figure 6e.

Position	Atom %	
	Ba	Al
Before hydration	27.5	72.5
1	37	63
2	35	65
3	28	72
4	30	70
5	27	73

resistance, reaching the limiting value within 38 h of exposure to 100% humid atmosphere, and for the sample with $x = 0.24$ the time required is 48 h.

Microstructural analyses

These studies were carried out with the intention of understanding more about the swelling process. The pellets having the composition $Ba_{0.76}Al_2O_{3.76}$, used for hydration studies, are subjected to the microstructural analyses. SEM micrographs have been taken after exposing the sample for different time intervals. Figure 6a shows the initial stage of the hydration wherein the compound reacted with water vapour, forming a fibrous swollen mass. The micrograph (Fig. 6a) clearly shows the change in volume as well as the morphology. As the exposure time is increased, the morphology of the compound formed changes to acicular as well as dendritic growth (Figs. 6b and c). Very long exposure resulted in selective growth of the hydration product on the surface of the pellet as shown in Figures 6d and 6e. These two figures are photographs taken at very low magnifications. Figure 6d shows the initial stage wherein the swollen part of the compound is slowly projecting out. With exposure time, the growth becomes more prominent all over the sample, as shown in Figure 6e. The product was subjected to elemental analyses using EDX, and the at% of Ba and Al present at various positions marked in Figure 6e are listed in Table 1. The data was collected across the growth direction. EDX analyses indicate barium enrichment towards position 1 and Al depletion in relation to position 5. These analytical data indicate migration of Ba^{2+} relative to Al^{3+} on micrometer levels. Elemental analyses are also indicative of the fact that the barium alumino hydroxy hydrate so formed also can accommodate the nonstoichiometry in composition. A micrograph taken after breaking the outwardly grown hydration product from the pellet surface (Fig. 6f) shows the acicular crystals projecting out from the pellet. As was the case with the powder, on long time exposure to humidity, the pellet was completely swollen and became powdery. The same results were obtained for the composition with $x = 0$ and $x = 0.56$. The observations remained consistent with different specimens of the same composition.

Discussion

The above results show that the nonstoichiometric barium orthoaluminates are highly reactive with water, and form a new hydration product. The hydration process is a solid/gas reaction followed by diffusion of constituents and crystallization of the products. The most important chemical reaction involved here is that of barium orthoaluminate with water vapour. Water molecules penetrate inside the grains through the structural channels, forming a gelly mass. The chemical constituents diffuse out to the grain surface and the hydration products are crystallised from this gelly mass. As a consequence, the volume of the solids within the original boundaries of specimen increases, resulting in a more voluminous mass. The reaction continues until there is no more barium orthoaluminate.

The observed results can be explained as follows: barium orthoaluminate belongs to the nepheline family (8), consisting of the framework of corner shared AlO_4 tetrahedra. This type of structure is known to have large open channels, which are occupied by cations of larger ionic radii. Nonstoichiometry can be explained in terms of the known crystal structure of the "stuffed" tridymite, nepheline and stoichiometric $BaAl_2O_4$. The stuffed tridymite structure can equally be considered as a member of the nepheline family, wherein the channels within the framework are partially filled by the larger cations, which leads to the nonstoichiometry (7). On hydration, Ba^{2+} ions occupying the channels will migrate in order to accommodate the incoming hydroxyl ions. As a result, the structure will rearrange and in the new form, Al^{3+} are in the octahedral rather than in tetrahedral sites of the starting composition, as revealed by the ^{27}Al MAS NMR results. The change in coordination number accompanying the hydration reaction enhances the molar volume, resulting in the swelling process. It is confirmed by the XRD results that the relative migration of the Ba^{2+} does not lead to phase separation into $Ba(OH)_2$ and $Al(OH)_3$ provided the reaction atmosphere is free of CO_2. If CO_2 is present in the reaction atmosphere, selective complexation of carbonate with Ba^{2+} takes place to form $BaCO_3$. The reaction rate in the case of the nonstoichiometric compositions is higher because of the structural vacancies, which makes diffusion of hydroxyl ions easier than in the stoichiometric composition. Thermal analyses shows that the reaction is completely reversible, indicating that the framework is not totally destroyed during the hydration process. On heating to 600°C, the hydroxyl groups in the framework are eliminated and the Ba^{2+} ions will migrate back into the channels, reconstituting the structure, because of the decreased mobility of Ba^{2+} in the anhydrous compounds.

Conclusions

Barium orthoaluminate with a general formula $Ba_{1-x}Al_2O_{4-x}$ $(0 < x < 0.56)$ reacts with water vapour to form a cementitious material, provided care is taken not to expose the material to CO_2 for long time. Once the gelly mass is formed, the humidity should be reduced below 50%; otherwise there will result the swelling of the material, forming a new compound and losing all its cementitious characteristics. The effect is very severe in presence of CO_2 plus moisture, forming $BaCO_3$ and aluminium hydroxide. The nonstoichiometric compositions react with water vapour faster than the stoichiometric sample.

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