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Synthesis and Characterization of a New Layered Barium Aluminate Containing Six-Membered Rings: $BaAl_2O_3(OH)_2 \cdot H_2O$

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A new layered barium aluminate hydrate, $BaAl_2O_3(OH)_2 \cdot H_2O$, has been synthesized from a hydrothermal system. The compound crystallizes in the orthorhombic space group *Pna*2_1 with $M = 291.33$, $a = 5.642(3)$ Å, $b = 9.887(7)$ Å, $c = 10.449(6)$ Å, $V = 582.9(6)$ Å^3, $Z = 4$, $R = 0.0288$, and $R_W = 0.0744$. The structure of the compound consists of aluminate sheets stacked in an ABAB sequence. Each individual sheet contains six-membered rings formed by corner-sharing $AlO_2(OH)_2$ tetrahedral units with the terminal OH groups pointing toward the interlayer region in one direction. There are Ba^{2+} cations and water molecules located between the adjacent aluminate sheets. On the basis of powder X-ray diffraction, the as-synthesized compound converts to the $BaAl_2O_4$ phase by thermal treatment at elevated temperatures. The phase transition has also been monitored by infrared spectroscopy. © 2001 Academic Press

Key Words: **hydrothermal synthesis; crystal structure; layered; barium aluminate.**

INTRODUCTION

Barium aluminates and their hydrates were prepared and investigated extensively in the past. They have been used for the formulation of refractory concrete, water purification, and as radiation-proof plaster (1). Recently, barium aluminates and the related hydrates were also used as binders for ceramics and refractories (2–4), light-cumulative fluorescent materials (5), and long afterglow phosphors (6). Ceria nanocrystals dispersed on the surface of barium hexaaluminate ($BaAl_{12}O_{19}$) is potentially applicable in ultra-clean catalytic combustion of methane (7), whereas the luminescence of rare-earth doped barium aluminates (8–11) have provoked considerable interest.

Most barium aluminates and their hydrates were structurally three-dimensional (12–17) and only three of them are one-dimensional (18–20). No two-dimensional structure for barium aluminates or their related hydrates has been reported yet in the literature. Monobarium aluminate dihydrate was first discovered by Carlson and Wells in 1948 (21). The compound was designated α-form by Thilo and Gessner in 1965 (22). In the mean time, a second polymorph (β-form) was found. γ-Monobarium aluminate dihydrate was prepared later on by Ahmed and Dent Glasser (23), and the structures of the α- and γ-polymorphs were also reported by these authors. However, the structure of the β-polymorph of monobarium aluminate remains unknown.

Here, we present the synthesis and structural characterization of a monobarium aluminate dihydrate which has the same formula as that for the α- and γ- polymorphs but has a completely different structural feature. Its structure consists of two-dimensional layers stacked in an ABAB sequence. Each individual layer is formed by six-membered rings of corner-sharing AlO_4 tetrahedra, and the barium atoms are located between the layers.

EXPERIMENTAL

To obtain the title compound, barium acetate ($Ba(CH_3COO)_2$) and sodium aluminate ($NaAlO_2$) were used as the barium and aluminum sources, respectively. Thus, sodium aluminate (1.9 g) and sodium hydroxide (0.3 g) were first added to water (20 ml), and the mixture was stirred until the solids were dissolved completely. To the solution barium acetate (1.0 g) was added with further stirring. The final reaction gel with a molar composition of 1:5.9:1.9:283 of $Ba(CH_3COO)_2{:}NaAlO_2{:}NaOH{:}H_2O$ was sealed in a Teflon-lined stainless steel autoclave and heated at 160°C for 3–7 days under autogenous pressure. The solid product was collected by filtration, washed copiously with distilled water, and dried at ambient temperature. The experimental density of the title compound was 3.34 g/cm^3, very close to the value (Table 1) obtained from the X-ray structural analysis. The effects of crystallization temperature and time on the product were investigated. It was found that the product appeared to be the known phase

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TABLE 1
Crystal Data and Structure Refinement for $BaAl_2O_3(OH)_2 \cdot H_2O$

Empirical formula	$H_4Al_2BaO_6$
Formula weight	291.33
Crystal system	Orthorhombic
space group	$Pna2_1$
a, Å	5.642(3)
b, Å	9.887(7)
c, Å	10.449(6)
V, Å^3	582.9(6)
Z	4
ρ_{cald}, g cm^{-3}	3.320
μ, cm^{-1}	70.72
λ, Å	0.71073
T, °C	20(2)
$F(000)$	536
Crystal size, mm	$0.3 \times 0.3 \times 0.3$
2θ range, °	5.68–46.10
Index ranges	$-6 \leq h \leq 6$, $-8 \leq k \leq 10$, $-9 \leq l \leq 11$
Total data collected	2560
Unique data	748
Final R indices	
R_1 $[I > 2\sigma(I)]$[a]	0.0288
wR_2 $[I > 2\sigma(I)]$[b]	0.0744
$\Delta\rho$ max/min e Å^{-3}	0.679 and -2.040

[a] $R_1 = \sum \| F_o| - |F_c \| / \Sigma |F_o|$.
[b] $wR_2 = [\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]]^{1/2}$.

$Ba_2Al_2O_5 \cdot 5H_2O$ when the temperature was above 180°C or when the reaction time was longer than 10 days with the temperature being kept at 160°C. If the crystallization temperature was lowered to 100°C, the product was α-$BaAl_2O_4 \cdot 2H_2O$.

The powder X-ray diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å). The inductive coupled plasma (ICP) analysis was conducted on a Perkin–Elmer Optima DV 3300 ICP spectrometer. The infrared spectra were recorded on a Nicolet Impact 410 FTIR spectrometer using KBr pellets.

A suitable triangular pyramid colorless single crystal of the title compound with dimensions of $0.3 \times 0.3 \times 0.3$ mm was glued to a thin glass fiber and mounted on a Bruker Smart CCD diffractometer equipped with a normal-focus, 2.4-kW sealed-tube X-ray source (graphite-monochromated Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. Intensity data were collected in 1271 frames with increasing ω (width of 0.30 per frame). Systematic absence and the statistics of intensity distribution resulted in the space group $Pna2_1$ (No. 33) for $BaAl_2O_3(OH)_2 \cdot H_2O$. The data processing was accomplished with the SAINT processing program (24). Direct methods were used to solve the structure using the SHELXTL crystallographic software package (25). The absorption correction was based on symmetry-equivalent reflections using the SADABS (26) program. Other effects such as absorption by glass fiber were simultaneously corrected. No indication of the hydrogen positions could be obtained. All non-hydrogen atoms were refined anisotropically. The crystallographic data are summarized in Table 1 and the atomic coordinates and selected bond distances and angles are listed in Tables 2 and 3, respectively.

TABLE 2
Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$)[a] for $BaAl_2O_3(OH)_2 \cdot H_2O$

Atom	x	y	z	U(eq)
Ba	1569(1)	5207(1)	3223(1)	13(1)
Al(1)	1496(5)	8373(3)	1645(3)	12(1)
Al(2)	1863(5)	1707(3)	1932(3)	12(1)
O(1)	1485(12)	10009(7)	2322(10)	19(2)
O(2)	1184(12)	8626(8)	− 26(8)	20(2)
O(3)	− 989(11)	7479(6)	2187(8)	15(2)
O(4)	1886(14)	4917(8)	361(10)	27(2)
O(5)	− 444(11)	2707(7)	2551(7)	14(1)
O(6)	2969(13)	7010(7)	5225(7)	17(2)

[a] U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

RESULTS AND DISCUSSION

Phase Identification

The ICP analysis indicates that the title compound contains 46.82 wt% Ba and 18.06 wt% Al, in good agreement

TABLE 3
Selected Bond Lengths (Å) and Angles (°) for $BaAl_2O_3(OH)_2 \cdot H_2O$

Ba–O(2)[a]	2.720(8)	Al(1)–O(3)[b]	1.745(7)
Ba–O(5)	2.809(7)	Al(1)–O(3)	1.752(7)
Ba–O(6)	2.859(7)	Al(1)–O(1)	1.765(8)
Ba–O(3)[b]	2.881(7)	Al(1)–O(2)	1.772(8)
Ba–O(3)	2.881(7)	Al(2)–O(3)[f]	1.745(8)
Ba–O(1)[b]	2.937(7)	Al(2)–O(5)[g]	1.750(7)
Ba–O(4)[c]	2.967(10)	Al(2)–O(5)	1.758(7)
Ba–O(4)	3.010(11)	Al(2)–O(6)[h]	1.811(8)
Ba–O(1)[d]	3.027(8)		

O(3)[b]–Al(1)–O(3)	107.5(3)	O(5)[g]–Al(2)–O(5)	108.7(3)
O(3)[b]–Al(1)–O(1)	108.4(4)	O(1)[f]–Al(2)–O(6)[h]	113.4(4)
O(3)–Al(1)–O(1)	109.3(4)	O(5)[g]–Al(2)–O(6)[h]	105.3(4)
O(3)[b]–Al(1)–O(2)	117.9(4)	O(5)–Al(2)–O(6)[h]	108.0(3)
O(3)–Al(1)–O(2)	108.1(4)	Al(2)[i]–O(1)–Al(1)	142.1(6)
O(1)–Al(1)–O(2)	105.4(4)	Al(1)[d]–O(3)–Al(1)	142.1(5)
O(1)[f]–Al(2)–O(5)[g]	109.8(4)	Al(2)[e]–O(5)–Al(2)	133.9(5)
O(1)[f]–Al(2)–O(5)	111.4(4)		

Note. Symmetry transformations used to generate equivalent atoms: [a] $-x + \frac{1}{2}, y - \frac{1}{2}, z + 1/2$; [b] $x + \frac{1}{2}, -y + \frac{3}{2}, z$; [c] $-x, -y + 1, z + \frac{1}{2}$; [d] $x - \frac{1}{2}, -y + \frac{3}{2}, z$; [e] $x - \frac{1}{2}, -y + \frac{1}{2}, z$; [f] $x, y - 1, z$; [g] $x + \frac{1}{2}, -y + \frac{1}{2}, z$; [h] $-x + \frac{1}{2}, y - \frac{1}{2}, z - \frac{1}{2}$; [i] $x, y + 1, z$.

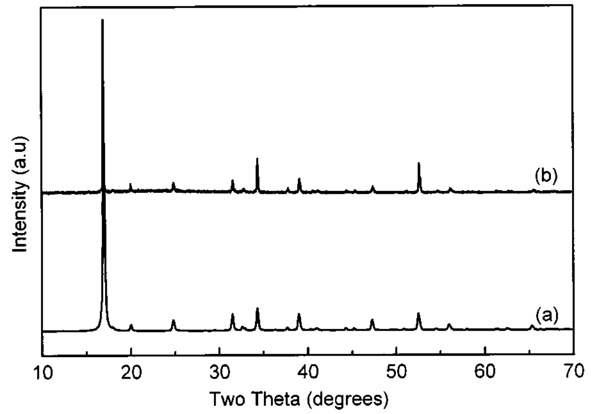

FIG. 1. Experimental (a) and simulated (b) powder X-ray diffraction patterns for $BaAl_2O_3(OH)_2 \cdot H_2O$.

with the values (47.14 wt% Ba, 18.52 wt% Al) based on the single-crystal structure analysis.

The powder X-ray diffraction pattern for $BaAl_2O_3(OH)_2 \cdot H_2O$ does not correspond to any known phase and the as-synthesized compound should be a structurally new material, although its empirical formula is the same as that of the α- and γ-forms of the monobarium aluminate dihydrate. The XRD pattern simulated on the basis of the single-crystal structure is in accordance with that of the experimental one. The diffraction peaks on both patterns correspond well in position, indicative of the phase purity of the as-synthesized sample (Fig. 1). The difference in reflection intensity between the simulated and experimental patterns is due to a certain degree of preferred orientation of the powder sample during data collection.

Structure Description

There are two crystallographically independent Al and one Ba atoms in the asymmetric unit of the title compound. The two crystallographically distinct Al atoms each share three oxygen atoms with adjacent Al atoms and the Al–O bond lengths vary within 1.741(8)–1.811(8) Å with the average value being 1.76 Å. This average bond length is slightly longer than that (ca. 1.74 Å) for other barium aluminates containing Al–O–Al bonds. The O1 atom is shared by Al1 and Al2, O3 by Al1 and Al1, and O5 by Al2 and Al2, respectively. The fourth oxygen atom on each independent Al atom is presumably associated with a hydrogen atom to satisfy the valence of the O atom. The bond lengths for the terminal Al–OH bonds are 1.772(8) and 1.811(8) Å, respectively. These values are in agreement with Al–OH bond lengths for the barium aluminate compounds reported previously (13). The bond angles of O–Al(1)–O and O–Al(2)–O vary from 105.3(4)° to 117.9(4)°. These bond angle values are close to those found for other barium aluminate hydrates (18, 19). The bond angles of Al–O–Al are within the range 133.9(5)°–142.1(6)°, which are smaller than those (147(1)°–156(1)°) (12) for the previously reported barium aluminate hydrates containing Al–O–Al bonds. The barium atom is coordinated by nine oxygen atoms at distances of 2.720(8)–3.027(8) Å (Fig. 2a). Of the nine atoms coordinating to each Ba atom, five are the Al-bridging O atoms, two are the O atoms of the terminal OH groups, and the remaining two are the O atoms of two water molecules. These Ba–O distance values are typical for Ba-containing oxide compounds (14, 18). The water molecule is H-bonded with two oxygen atoms of the terminal OH groups, and the $O_4 \cdots O_2$ (2.849 Å) and $O_4 \cdots O_6$ (2.879 Å) distances are typical for H-bonds (Fig. 2b).

The structure of the title compound has a layer feature. Unlike aluminosilicates (27, 28) and aluminophosphates (29–31), aluminates that possess a layered structure are not common. In the title compound, tetrahedral AlO_4 primary units are corner-shared to form infinite aluminate sheets. The primary units are connected in such a way that edge-sharing six-membered T-rings (T stands for Al) are en-

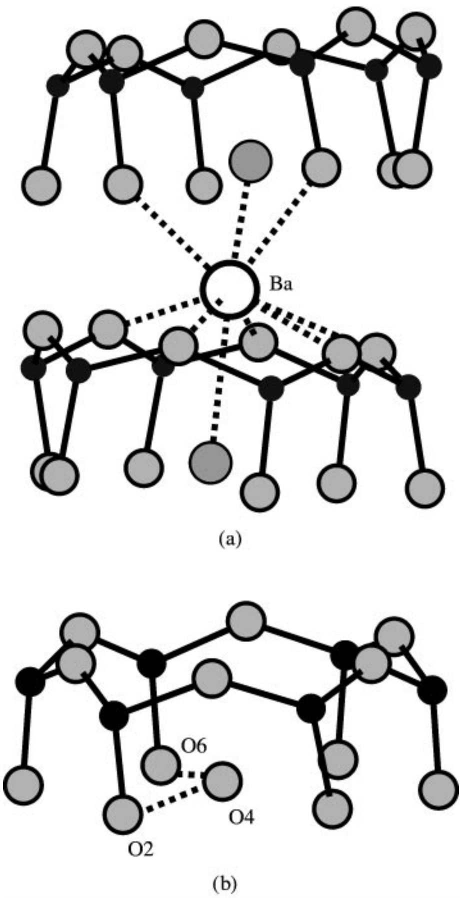

FIG. 2. The situation for (a) the coordination of the Ba atom and (b) the hydrogen bonds for the water molecule between adjacent aluminate sheets.

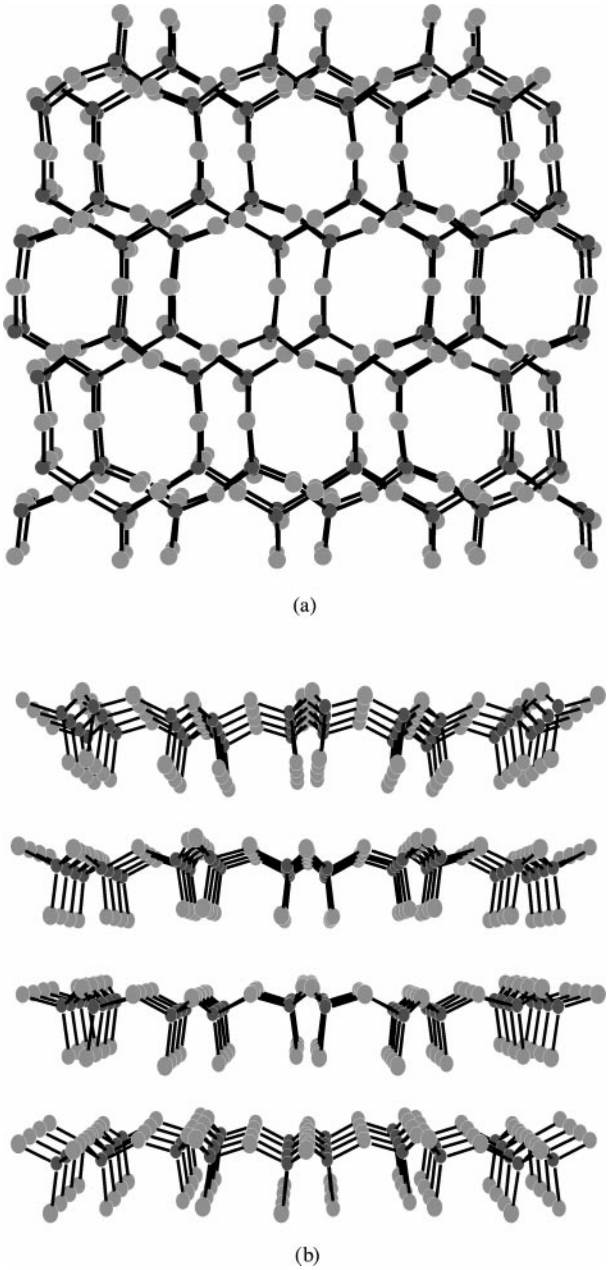

FIG. 3. Network structure of $BaAl_2O_3(OH)_2 \cdot H_2O$ viewed along (a) the [001] and (b) the [100] directions. For clarity, the Ba atoms and the O atoms of the water molecules are not shown.

visaged in the individual sheet and the terminal Al–OH bonds point toward the interlayer region in one direction (Fig. 3). The Ba atoms are located between the aluminate sheets with H_2O molecules coordinating from the top and the bottom of the atoms. It is interesting to note that the stacking of the aluminate layers in the title compound is in an ABAB sequence (31–34) along the crystallographic *c* axis. Namely, the atoms in the first layer are in the same positions as the corresponding ones in the third layer whereas the atoms in the second layer coincide with those in the fourth layer if the structure is viewed along the *c* axis. There are two layers in each stacking period for the title compound.

Of the barium aluminates and their related hydrates, the majority are structurally three-dimensional, and only a few are of one dimension. Among the one-dimensional barium aluminates are α- and γ-$BaAl_2O_3(OH)_2 \cdot H_2O$, and the common structural feature for these 1-D compounds is that each aluminum atom is coordinated tetrahedrally by four oxygen atoms and the AlO_4 tetrahedra are linked by sharing corners to form chains. The molecular formula of the title compound is the same as that of the one-dimensional barium aluminates α- and γ-$BaAl_2O_3(OH)_2 \cdot H_2O$ but the structure of it is of two dimensions. For the alkaline-earth metal aluminates and related hydrates there are three types of known layer structures. The structure of $SrLa_2Al_2O_7$ (35) is isostructural with $Sr_3Ti_2O_7$ in which TiO_2 and SrO form alternating layers. However, the coordination number of Al in $SrLa_2Al_2O_7$ is six instead of four. In the $CaSmAlO_4$ (36) structure, the individual layer consists of a network of edge-sharing four-membered rings with each ring being formed by four corner-sharing AlO_6 octahedra. Another layered aluminate is $Ca_5Al_6O_{14}$ (37) in which the individual layer is a 2D network of edge-sharing five-membered rings with each ring being formed by five corner-sharing AlO_4 tetrahedra. The title compound is a barium aluminate with an unusual layer structure, and its structure feature is rather distinct from those three types of layer structures for the known alkaline-earth metal aluminates mentioned above.

Thermal Properties

The thermogravimetric analysis shows a major weight loss occurring at about 280°C, and following this major weight loss, the compound further loses its weight gradually up to 700°C. The total weight loss between 240 and 700°C is about 15%, close to the value calculated on the basis of the empirical formula (6.2% for dehydration and 6.2% for dehydroxylation). The weight loss (about 4.5%) occurring from 30 to 240 is at least partly due to disordered water molecules contained in the title compound. The title compound calcined in air at various temperatures was monitored by powder X-ray diffraction (Fig. 4). It is found that the material shows a phase transition at 300–400°C. The diffraction intensity of the compound decreases to a considerable extent after heating at 300°C for 2 h. When the thermal treatment temperature is raised to 400°C, the compound converts to $BaAl_2O_4$ (15). The diffraction intensity increases with the heating temperature, indicative of crystallinity enhancement of the newly formed barium aluminate compound at elevated temperatures (Fig. 4c–g). Previously, the $BaAl_2O_4$ compound was synthesized by a solid-state method, and a temperature as high as 1200°C was needed for the synthesis, whereas the same $BaAl_2O_4$

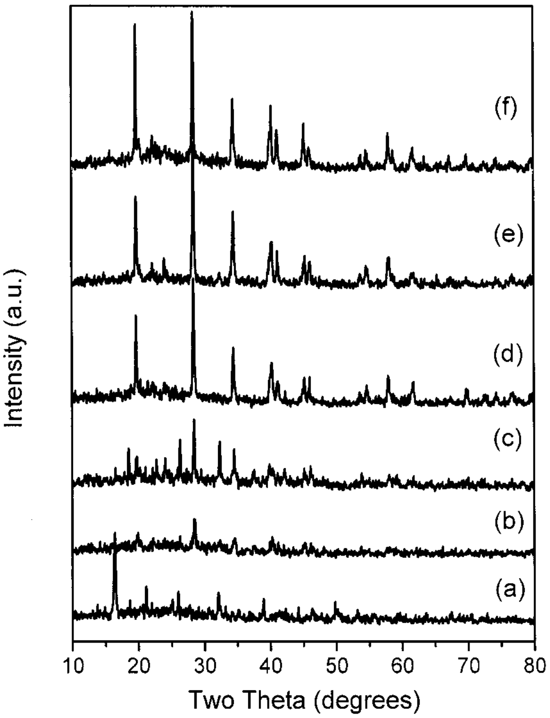

FIG. 4. Powder X-ray diffraction patterns of $BaAl_2O_3(OH)_2 \cdot H_2O$ calcined at various temperatures: (a) 300°C; (b) 400°C; (c) 500°C; (d) 600°C; (e) 700°C; (f) 800°C.

compound with good crystallinity can be obtained by heating at 600°C from the title compound as a precursor.

The IR spectrum of the title compound is shown in Fig. 5a. The bands at 3460 and 3560 cm^{-1} are attributed to stretching vibrations of OH groups, whereas those at 1636 and 1440 cm^{-1} are due to deformative modes of water molecules. There are also absorptions at 900–500 cm^{-1} associated with the stretching vibrations of AlO_4 units. The absorption at about 900 cm^{-1} is assigned to the stretching vibrations of Al–O–Al bonds, whereas those at about 680 cm^{-1} are attributable to the vibrations of terminal Al–OH bands (23). The IR spectra of the compound calcined in air at various temperatures are shown in Fig. 5b–e. It is found that the bands at 3460, 3560, and 1636 cm^{-1} disappear with increasing temperature. But there is not much change in the absorptions from 900 to 500 cm^{-1}. This confirms that the title compound converts to the $BaAl_2O_4$ phase that has no H_2O molecules and hydroxyl groups.

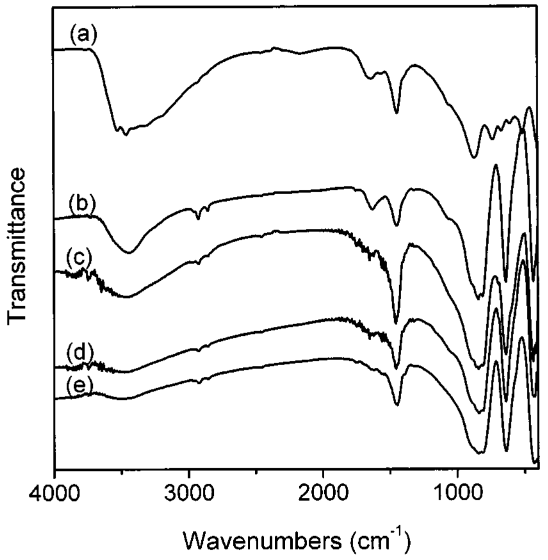

FIG. 5. Infrared spectra of $BaAl_2O_3(OH)_2 \cdot H_2O$ within 400–4000 cm^{-1} before and after thermal treatments: (a) as-synthesized; (b) 300°C; (c) 400°C; (d) 600°C; (e) 800°C.

CONCLUSIONS

A new layered barium aluminate hydrate ($BaAl_2O_3(OH)_2 \cdot H_2O$) crystallizes under hydrothermal conditions. X-ray structural analysis shows that the compound is composed of aluminate sheets stacked in an ABAB sequence with each individual sheet containing six-membered rings formed by corner-sharing AlO_4 tetrahedral units. The title compound converts to $BaAl_2O_4$ phase by thermal treatments at elevated temperatures.

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