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Synthesis and characterization of gel-derived barium hexa-aluminate

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Transparent barium hexa-aluminate gel was synthesized by chemical polymerization reactions involving commercial aluminium di(isopropoxide) acetoacetic ester and barium acetate. The gel was evaluated in terms of weight loss and thermal and crystallization characteristics by thermogravimetric analysis, differential thermal analysis, transmission electron microscope and X-ray diffraction. The as-prepared gel was amorphous to electron diffraction. X-ray diffraction results showed that fully crystalline barium hexa-aluminate can be produced at $\leqslant 1200^\circ$ C which is 150° C less than the minimum synthesis temperature reported in the literature. The crystallization kinetics of the gel are discussed on the basis of the X-ray diffraction data. Furthermore, preliminary studies were conducted to examine the sintering behaviour of isostatically pressed pellets fabricated from 800° C heat-treated and milled gel powder. The sintered pellets were characterized in terms of density, microstructure, and linear thermal expansion. Sinterability of the material at 1550° C was unsatisfactory. The sintered density of the pellets was less than 60%. Microstructural examinations showed that sintered pellets were highly porous and consisted of a mixture of round, hexagonal plate-like and needle-like particles, the relative proportion of each type being dependent on the heat-treatment schedule. The linear expansion coefficient measured on a 1550° C sintered specimen was 7.3×10^{-6} in the 15 to 1000° C range.

1. Introduction

The existence of three stoichiometric barium aluminates has been reported in the literature [1]; namely, tribarium aluminate, $3BaO \cdot Al_2O_3$; barium monoaluminate, $BaO \cdot Al_2O_3$, and barium hexa-aluminate, $BaO \cdot 6Al_2O_3$ with melting points at 1750, 1830 and 1900° C, respectively. Although the importance of barium aluminate materials has been recognized in the context of producing refractory cement and concrete [1], the potential of these materials for fabricating structural and/or electrical ceramics has not been explored. Cement researchers have shown particular interest in barium monoaluminate because (1) it has good hydraulic hardening properties [1–3], (2) it contributes to high early strength, increased refractoriness, and mechanical strength of the cement [1–3], and (3) barium monoaluminate bearing cement may also have possible applications in providing refractory concrete for efficiently shielding atomic reactors at high temperature [4]. Barium hexa-aluminate, which is the most refractory among the barium aluminate materials, has not attracted much interest in cement research, because it has no binding properties [5] and, furthermore, it has been documented that the presence of barium hexa-aluminate causes lower strengths in cements [6]. Synthesis and physiochemical characterization of barium hexa-aluminate has been reported by Semin *et al.* [7], but the results of these studies could not be obtained. Other interests in barium hexa-aluminate include the electrical phenomena [8] in doped single-crystal thin films. According to Semin *et al.* [7], the preparation method for barium and some other alkaline earth hexa-aluminates is optimum when the reactants are coprecipitated. Chandra [5] has synthesized high-purity barium hexa-aluminate at 1350° C using a powder mixture of alumina (Al_2O_3), barium carbonate ($BaCO_3$), and 25% extra hydrated barium chloride ($BaCl_2 \cdot 2H_2O$). In this synthesis approach a low-melting $BaCO_3$–$BaCl_2$ eutectic formed at 840° C accelerates the reaction and, as a result, barium hexa-aluminate is formed at much lower temperature than in the conventional method [1] where a temperature in excess of 1600° C may be required.

To our knowledge the properties of barium hexa-aluminate as a ceramic material have not been studied systematically. Therefore, the primary objective of the present study was to examine the suitability of barium hexa-aluminate as a ceramic material. In our study, the sol–gel process was adopted for synthesizing this material in consideration of chemical and microstructural homogeneity of the final ceramic [9, 10].

2. Experimental procedure

2.1 Starting chemicals

Commercially available, reagent-quality chemicals were used – 95% aluminium di (isopropoxide) acetoacetic ester chelate, $Al(OC_3H_7)_2(C_6H_9O_3)$ (Morton Thiokol, Inc., Danvers, Massachusetts) and barium carbonate, $BaCO_3$ (J. T. Baker Chemical Company, Phillipsburg, New Jersey) were the precursors for

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aluminium oxide, Al_2O_3 and barium oxide, BaO, respectively. Glacial acetic acid, CH_3COOH, and 1-butanol, $CH_3(CH_2)_3OH$ (Morton Thiokol) were ACS reagent grade.

Aluminium alkoxyester chelate was chosen as the precursor material for aluminium oxide instead of an aluminium alkoxide for two reasons. First, the alkoxyester chelate hydrolyses at a lower rate than the aluminium alkoxides [11] and the chemical polymerization can be reasonably well controlled. The increased hydrolytic stability of aluminium alkoxyester (compared to aluminium alkoxide) may be due to a chelation effect and/or steric hindrance offered by the large acetoacetic ester radial. Second, the selected aluminium alkoxyester chelate is commercially available in bulk quantities.

Even though anhydrous barium acetate is commercially available, we used barium carbonate as the source of barium oxide and neutralized it with acetic acid to produce barium acetate. This was done because commercially available barium acetate may contain an amount of barium acetate monohydrate, $Ba(OOCCH_3)_2 \cdot H_2O$ thus affecting the stoichiometry of the starting composition.

2.2. Gel preparation

In a plastic beaker, 125.8 g aluminium di(isopropoxide) acetoacetic ester chelate dissolved in 1-butanol to a volume of 900 ml. In a second (glass) beaker 7.5426 g barium carbonate was neutralized with a minimum amount of glacial acetic acid and boiled to remove completely any dissolved carbon dioxide. The total volume of the barium acetate solution thus prepared was 75 ml. The barium acetate solution was cooled, then added to the solution of aluminium di (isopropoxide) acetoacetic ester chelate and stirred for 5 min. Subsequently, 25 ml distilled water was added slowly to the solution mixture under vigorous stirring. The resulting clear solution (pH ~ 5.5) formed a transparent gel in about 10 h at ambient temperature. The gel was dried in an air oven at 70° C for about 2 weeks and then ground in an agate mortar to produce dry gel powder.

2.3. Gel characterization

The barium hexa-aluminate gel was evaluated in terms of its thermal and crystallization behaviours. The thermal behaviour was examined by thermal gravimetric (TGA) and differential thermal (DTA) analyses. For both TGA and DTA the powdered gel specimens, previously dried at 70° C, were heated at a rate of $50° C h^{-1}$ in a free-flowing oxygen environment. The crystallinity of the as-prepared gel was examined by electron diffraction analysis using a Jeol JEM 100B scanning transmission electron microscope (Japan Electron Optic Co.). The specimen was prepared using a drop of suspension ultrasonically dispersed in anhydrous ethanol on a carbon-coated grid. For crystallization studies, the gel powders were heated (heating rate $50° C h^{-1}$) for 2 h at 300, 800, 1200 and 1500° C in the ambient atmosphere and examined by an X-ray diffraction (XRD) method (Cu*Kα* radiation) using a computer-controlled Rigaku X-ray diffractometer provided with a peak search attachment.

2.4. Fabricating and characterizing barium hexa-aluminate ceramic

The gel powder was heated at 800° C for 4 h in an ambient atmosphere to remove the residual organics and structural water, wet-milled in acetone using alumina balls, then dried in an air oven at 110° C overnight. From this milled powder, a number of "green" pellets were dry-formed by isostatic pressure of 346 MPa. Initially, thermal dilatometric analysis (TDA) up to 1500° C was performed on a "green" pellet at a heating rate of $50° C h^{-1}$ to examine the sintering characteristics of the pellet. Subsequently, the pellets were sintered at 1300° C for 2 h and at 1550° C for 2 h and for 24 h.

The sintered pellets were evaluated in terms of density, microstructure, and thermal expansion characteristics. Density was measured from weight and dimensions of the pellet. Thermal expansion characteristics were measured on a 5.08 cm rod specimen using an Orton Automatic Recording Dilatometer. For microstructural studies the fracture surfaces of the pellets were gold-coated and examined by scanning electron microscopy.

3. Results and discussion

3.1. Gel preparation

Barium hexa-aluminate gel was prepared at ambient temperature by chemical polymerization reactions involving aluminium di (isopropoxide) acetoacetic ester chelate and barium acetate in the presence of water. Approximately 9 mol water were used per mole of the aluminium alkoxyester and the solution concentration (i.e. grams barium hexa-aluminate per 100 ml) was approximately 3%. The gelling time (which was about 10 h) can be significantly reduced by increasing the solution concentration and/or the molar ratio of water. For example, with a 7% solution containing 12 mol water per mole aluminium alkoxyester gelled in less than 1 min.

The sequence of reactions that leads to the formation of barium hexa-aluminate gel may be very complex. However, it is speculated than when an aqueous or an aqueous-alcoholic solution of barium acetate is added to the solution of aluminium alkoxyester chelate the alkoxy groups (i.e. OC_3H_7 groups) of the alkoxyester are first replaced by hydroxyl groups (i.e. OH groups) by hydrolyses followed by homo- or polycondensation reactors to form macromolecules containing Al–O–Al bridges (i.e. metalloxane chains). As the hydrolytic polycondensation reactions of aluminium alkoxyester proceeds, barium ions present in the solution are also incorporated into the structure – leading finally to the formation of barium hexa-aluminate gel. It seems quite probable that barium atoms are linked to the metalloxane chains by predominantly ionic bonds.

3.2. Gel characterization

3.2.1. Electron diffraction analysis

The electron diffraction pattern of the as-prepared gel

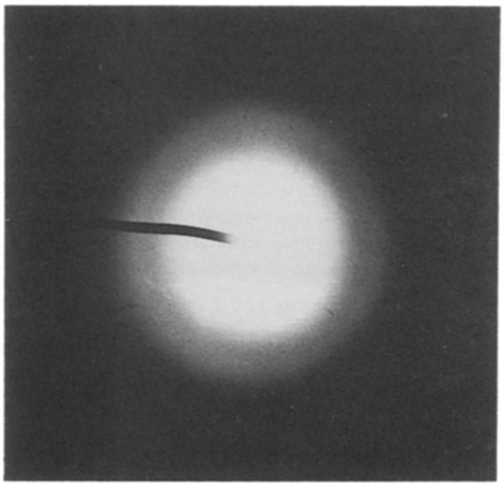


Figure 1 Electron diffraction pattern of as-prepared barium hexa-aluminate gel.

produced a diffused band (Fig. 1) which indicates that the material was amorphous.

3.2.2. Thermal gravimetric analysis (TGA)

The TGA of dried gel powder in an oxidizing atmosphere (Fig. 2) showed a 56.8% weight loss up to 600° C which may be attributed to loss of chemisorbed water and organics such as acetic acid, propyl acetate, residual structural alkoxide and acetoacetic ester, etc. A further weight loss of 2.0% that took place between 700 and 820° C may represent decomposition of $BaCO_3$ formed *in situ* (as will be seen later in XRD data) during the thermal decomposition of organics. No further weight loss took place beyond 820° C.

3.2.3. Differential thermal analysis (DTA)

Fig. 3 shows the DTA curve of the dried barium hexa-aluminate gel powder. The curve shows two large overlapping exotherms with peaks at 220 and 290° C, a small endothermic peak at 780° C, and a broad exotherm with the peak at 1230° C. The first two exotherms occurred in the temperature range at which most of the weight loss occurred (Fig. 2). The two exotherms may represent either oxidation of two different types of organics or oxidation as well as crystallization of the gel. An endotherm corresponding to loss of chemisorbed water, if present, was not detected in this temperature range, which could be due to a masking effect of the exotherms. The endothermic peak at 780° C, which is also associated with weight loss (Fig. 2), could represent decomposition of $BaCO_3$ formed *in situ*. The broad exotherm, which starts around 800° C, may represent the crystallization process. Thus, the TGA and DTA results were consistent.

3.2.4. X-ray diffraction analysis (XRD)

X-ray diffraction studies were conducted on barium hexa-aluminate gel, heated for 2 h each at 300, 800 and 1200° C. The choice of heat-treatment temperatures was based on the DTA results. The XRD patterns together with lattice parameters of 300, 800 and 1200° C heat-treated specimens are shown in Fig. 4, 5 and 6, respectively. The 300° C heat-treated specimen showed a diffraction pattern (Fig. 4) identical to $BaCO_3$ (JCPDS Card no. 50378), the diffraction pattern of the 800° C heat-treated specimen corresponds to that of barium monoaluminate, $BaAl_2O_4$ (JCPDS Card no. 170306), and that of the 1200° C heat-treated specimen corresponds to that of barium hexa-aluminate, $BaAl_{12}O_{19}$ (JCPDS Card no. 140107).

The formation of barium carbonate during the 300° C heat treatment of the barium hexa-aluminate gel could be explained on the assumption that carbon dioxide and water (evolved during thermal degradation of the organics) could react with the barium ions to produce barium carbonate. The 800° C heat-treated specimen showed the presence of $BaAl_2O_4$ only; which means that the excess alumina (in excess of $BaAl_2O_4$ composition) present in the barium hexa-aluminate gel did not crystallize at this temperature even though pure alumina gel is expected to crystallize at about 500° C [12]. Therefore, the crystallization of $BaAl_2O_4$ in preference to Al_2O_3 may be related more to

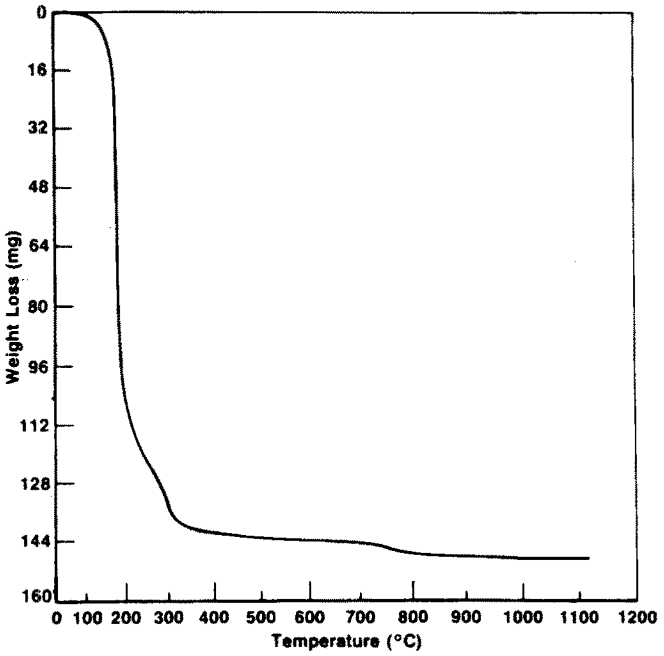


Figure 2 TGA curve of barium hexa-aluminate gel. Sample size 253.6 mg; heating rate 50° C h^{-1}; atmosphere 2 cfh oxygen; type 5 thermocouple.

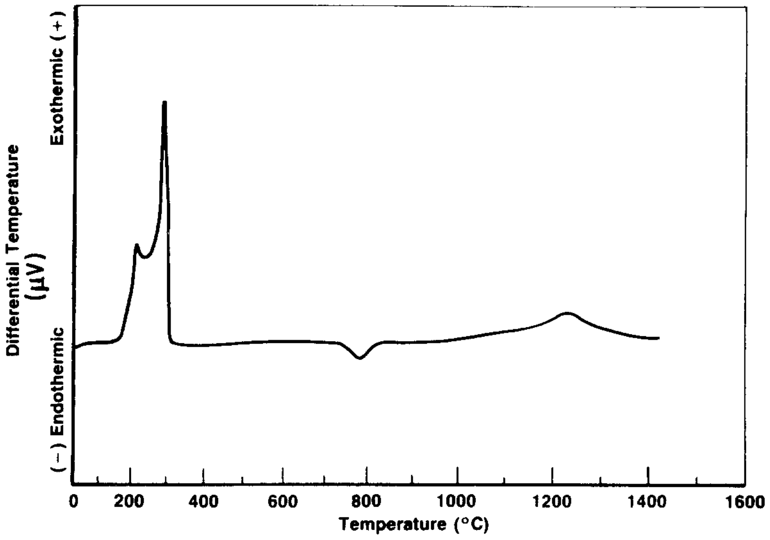


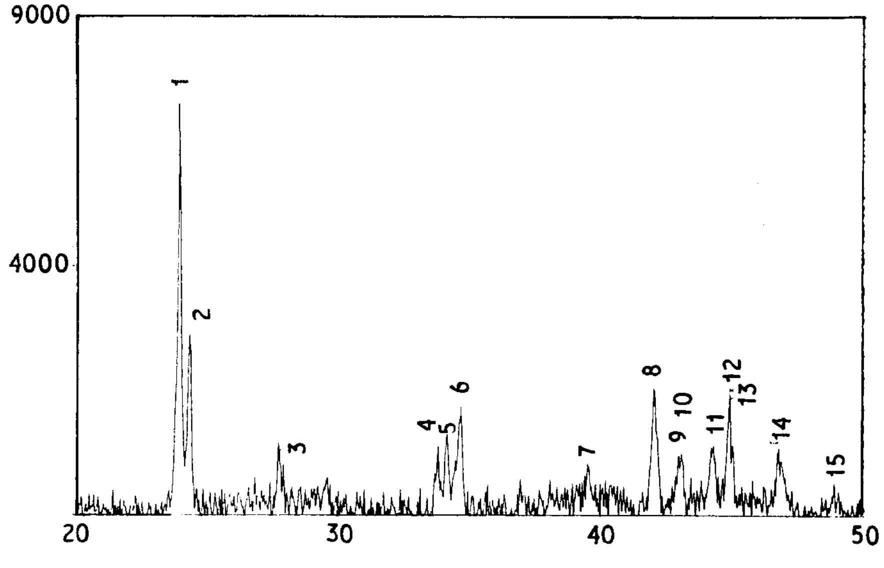
Figure 3 DTA curve of barium hexa-aluminate gel. Sample size ~300 mg; heating rate 50° C h^{-1}; atmosphere 5 cfh oxygen, type S thermocouple.

kinetic than thermodynamic factors. The broad exotherm in the DTA curve (Fig. 3) that initiates just beyond 800° C perhaps indicates initiation of the diffusion process. However, note that the DTA curve did not show the exothermic peak around 800° C that corresponds to crystallization of $BaAl_2O_4$, most likely due to masking effect of the endothermic peak corresponding to the loss of CO_2 resulting from the decomposition of $BaCO_3$.

3.3. Fabrication and characterization of barium hexa-aluminate ceramic

3.3.1. Sintering behaviour

Fig. 7 shows the thermal dilatometric analysis (DTA) curve obtained with an isostatically pressed (345 MPa) pellet. A 9.2% linear shrinkage of the pellet was indicated in the TDA curve (starting at about 800° C) up to 1200° C. A small shrinkage (about 0.6%) was also indicated in the 1460 to 1500° C range.



No.	2θ (deg)	Intensity	*d*	FWHM	I/I_0
1	23.94	503	3.713	0.21	100
2	24.32	219	3.656	0.21	43
3	27.98	55	3.186	0.135	10
4	33.8	86	2.649	0.12	17
5	34.1	81	2.626	0.18	16
6	34.68	135	2.584	0.105	26
7	39.5	57	2.279	0.15	11
8	42.04	156	2.147	0.12	31
9	43	74	2.101	0.135	14
10	43.12	76	2.096	0.15	15
11	44.26	85	2.044***		16
12	44.96	139	2.014	0.12	27
13	45.06	87	2.01	0.165	17
14	46.84	83	1.937***		16
15	48.94	41	1.859***		8

Figure 4 X-ray diffraction pattern of barium hexa-aluminate gel, heat treated at 300° C/2 h in air.

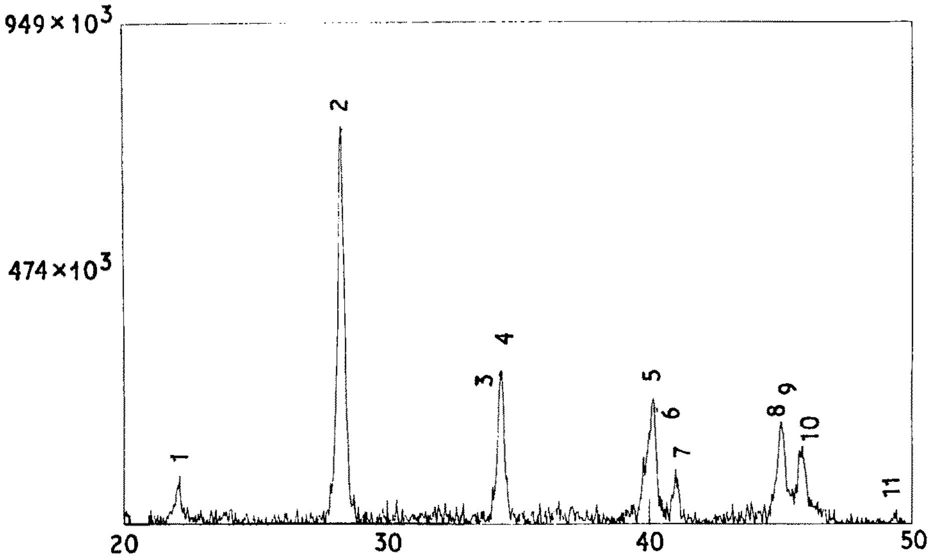


Figure 5 X-ray diffraction pattern of barium hexa-aluminate gel, heat treated at 800° C/2 h in air.

No.	2θ (deg)	Intensity	d	FWHM	I/I_0
1	22.14	96	4.011***		12
2	28.28	759	3.152***		100
3	34.24	244	2.616	0.135	32
4	34.38	268	2.606	0.15	35
5	40.1	234	2.246	0.21	30
6	40.28	129	2.237	0.15	16
7	41	106	2.199		13
8	45.02	182	2.011	0.18	23
9	45.16	162	2.006	0.135	21
10	45.74	139	1.981	0.105	18
11	49.42	28	1.842***		3

On the basis of the TDA results, a number of pellets were sintered at 1300° C/2 h, 1550° C/2 h, and 1550° C/24 h. After sintering at 1550° C/2 h, the bulk density of the pellets was about 60%. It was clear that the sinterability of the material at the experimental temperature is poor. Therefore, special sintering techniques (such as hot pressing and/or hot isostatic pressing) would be required to produce high-density ceramic bodies at lower temperatures.

3.3.2. *Microstructures*

The scanning electron photomicrographs of the fracture surfaces of pellets sintered at different temperatures and times are shown in Figs 8 to 10. Microstructures of all the sintered specimens showed a highly porous structure. The most unexpected feature was the nonuniformity of the grain morphology (i.e. size distribution and shape of the grains) and the nature of the grain growth as sintering temperature and time were increased. The microstructure of the 1300° C/2 h heat-treated specimen generally consisted of round grains (Fig. 8) of about 0.13 to 0.25 μm diameter; however, at 1550° C/2 h, grain coarsening resulted in a dramatic change of grain morphology (Fig. 9) such that the microstructure was mainly composed of two types of randomly oriented grains; plate-like grains with no well-defined facets, and sharp-edged needle-like grains (aspect ratio ~2 to 6.5). The size of the plate-like grains could not be measured due to their orientations. Whilst most of the needle-shaped grains looked like projected plates, a few of them showed the presence of nodules. A longer holding time (24 h) at 1550° C produced further changes in grain morphology (Fig. 10). In these specimens some of the plate-like grains were clearly hexagonal and the needle-like grains appeared to be smooth and of uniform texture.

3.3.3. *Linear thermal expansion*

The linear thermal expansion curve of a 1550° C/2 h heat-treated, 5.08 cm rod specimen measured up to 1000° C is shown in Fig. 11. The specimen was heated at 100° C h^{-1} in air environment. The calculated coefficients of linear thermal expansion (α) were as follows ($\times 10^{-6}$): $\alpha_{15\text{-}100}$4.82, $\alpha_{15\text{-}150}$5.18, $\alpha_{15\text{-}200}$5.89, $\alpha_{15\text{-}500}$6.43 and $\alpha_{15\text{-}1000}$7.3. Note however, that the thermal expansion coefficient of fully dense barium hexa-aluminate ceramic could be significantly different.

4. Conclusions

The following conclusions can be drawn on the basis of the experimental results.

1. By taking the sol–gel approach, barium hexa-aluminate can be synthesized at 1200° C which is 150° C less than the minimum synthesis temperature reported in the literature.

2. The crystallization process of the sol–gel-derived material involved the formation of barium monoaluminate as an intermediate phase prior to the conversion into barium hexa-aluminate.

3. The sinterability of barium hexa-aluminate was unsatisfactory up to 1550° C/24 h. Pressureless

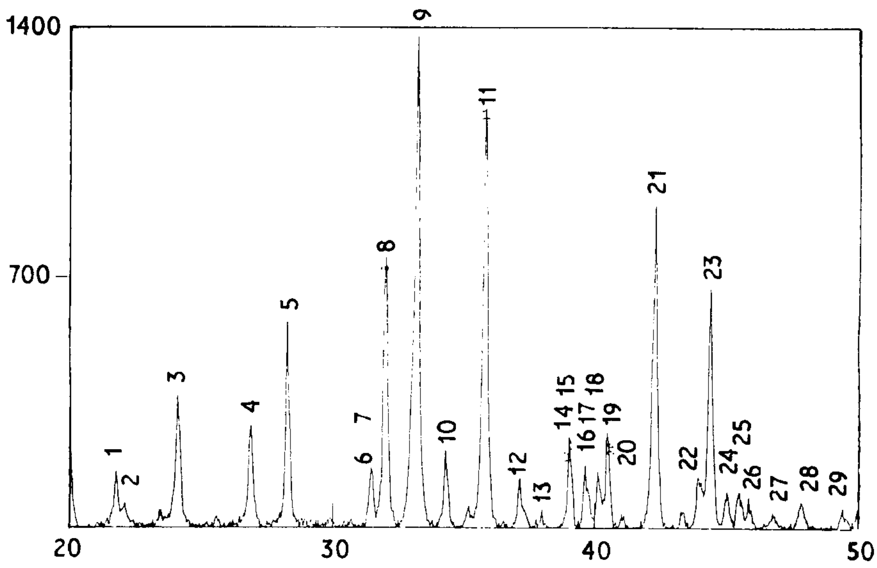


Figure 6 X-ray diffraction pattern of barium hexa-aluminate gel, heat-treated at 1200° C/2 h in air.

No.	2θ (deg)	Intensity	d	FWHM	I/I_0
1	21.78	159	4.077***		11
2	22.12	71	4.015	0.12	5
3	24.14	372	3.683	0.24	26
4	26.88	280	3.313	0.24	20
5	28.3	582	3.15	0.24	41
6	31.42	135	2.844	0.105	9
7	31.48	169	2.839	0.15	12
8	31.98	666	2.796	0.3	48
9	33.2	1387	2.696	0.33	100
10	34.28	192	2.613	0.18	13
11	35.76	1089	2.508	0.3	78
12	37.08	108	2.422	0.195	7
13	38	56	2.365	0.12	4
14	38.98	126	2.308	0.18	9
15	39.2	90	2.296	0.135	6
16	39.64	172	2.271	0.15	12
17	39.76	111	2.265	0.105	8
18	40.12	160	2.245	0.12	11
19	40.46	242	2.227	0.27	17
20	40.66	78	2.217	0.12	5
21	42.28	907	2.135	0.21	65
22	43.98	121	2.058	0.12	8
23	44.38	643	2.039	0.18	46
24	45.08	98	2.009	0.15	7
25	45.42	67	1.995	0.135	4
26	45.88	87	1.976***		6
27	46.8	46	1.939***		3
28	47.88	76	1.898***		5
29	49.4	57	1.843	0.12	4

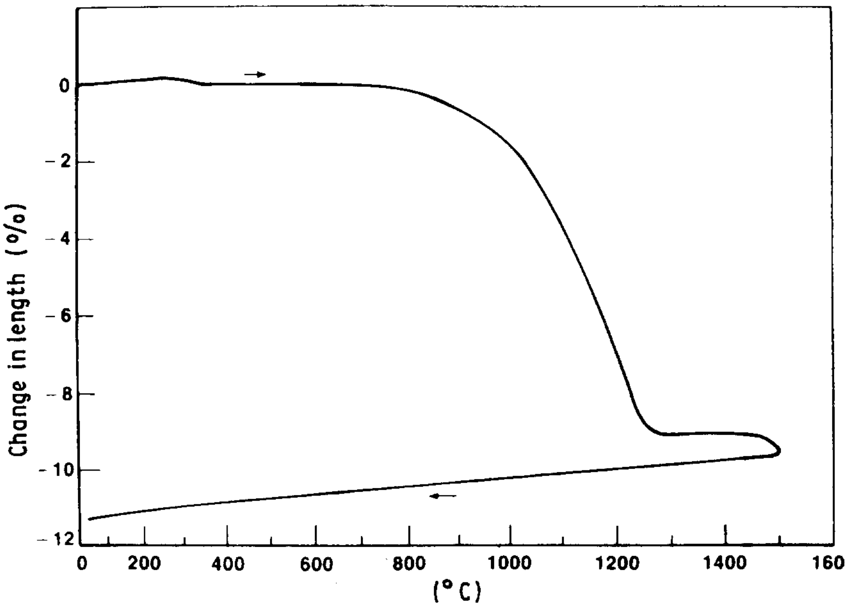


Figure 7 TDA curve of isostatically pressed pellet fabricated with 800° C heat-treated barium hexa-aluminate gel powder. Pellet size 12.8 mm; heating rate 50° C h^{-1}; atmosphere, static air; type S thermocouple.

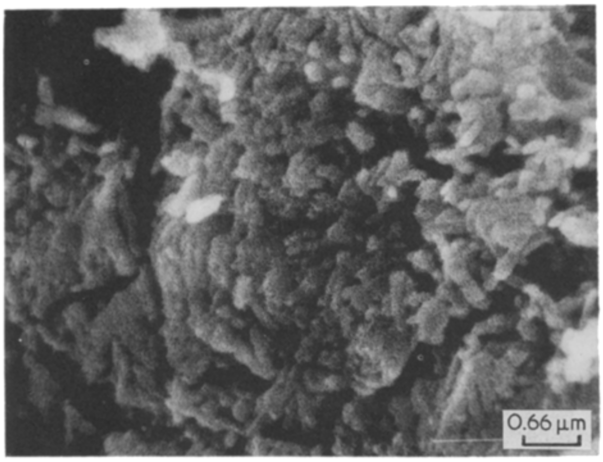


Figure 8 Scanning electron micrograph of the fractured surface of the specimen after heat treatment at 1300° C/2 h.

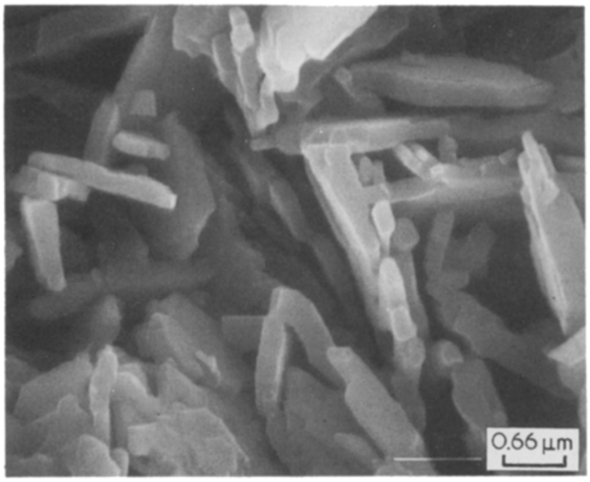


Figure 9 Scanning electron micrograph of the fractured surface of the specimen after heat treatment at 1500° C/2 h.

sintering of isostatically pressed specimens produced highly porous ceramic bodies.

4. Depending on the heat-treatment schedule, the sol–gel-derived material produced grains of three different shapes (i.e. round plate-like, and needle-like) of width size distribution.

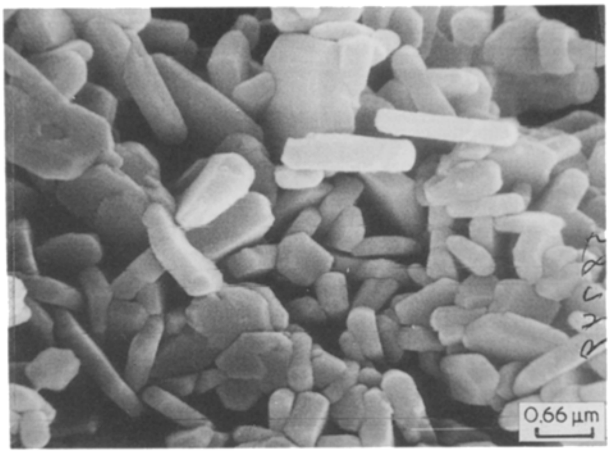


Figure 10 Scanning electron micrograph of the fractured surface of the specimen after heat treatment at 1550° C/24 h.

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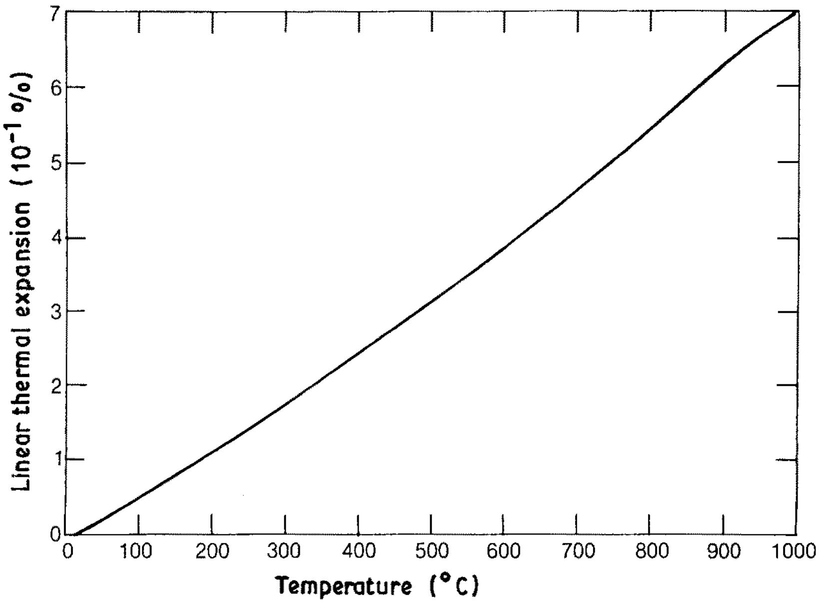

Figure 11 Thermal expansion curve of barium hexa-aluminate ceramic sintered at 1550° C/2 h.

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