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Structural evolution in alumina gel

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Thermal treatment and consequent dehydration modifies the structure of boehmite gel, which transits from a polymeric, partially disordered state to the crystalline α-alumina via several transition phases. We have investigated the evolution of the microstructure and structural order in the lattice. The significance of particle morphology is brought out in the sintered gel powder pellet. The transparency of the gel glass, despite the large porosity confirms the absence of long range order upto the δ-phase.

1. Introduction

Transparent ceramic oxides can be prepared from metal alkoxides using the sol-gel technique [1]. The dried gel, a precursor of transparent ceramic, can yield very fine powder or a monolith glass of high reactivity. We had earlier studied the transmission properties of transparent alumina monoliths and found that the dehydration of the glassy xerogel was accompanied by phase transformations and consequent structural changes [2]. We report here our investigation on the evolution of structural order and the control of microstructure in densification and grain growth. We have followed the sequence of dehydration with different physical measurements namely infrared absorption, X-ray diffraction (XRD) and microstructural changes. The use of Mo$K\alpha$ radiation for X-rays has been advantageous in categorizing the structure of γ-alumina.

2. Experiment and results

2.1. Preparation of the material

The samples were prepared by the hot water hydrolysis of aluminium isopropoxide with hydrochloric acid as the catalyst following a method described by Yoldas [1]. The temperature of hydrolysis was 80° C. The alkoxide to water to acid molar ratio was kept as 1 : 100 : 0.3. The concentration of the clear sol led to gelation. The powders were obtained by dehydrating the gel, whereas the monolithic transparent glasses were prepared by the slow evaporation of the hydrated gel. A controlled evaporation over a period of time was absolutely essential for obtaining crack-free, clear discs, 3 to 5 cm in diameter and 1 to 2 mm thick. The microstructure of the dry gel (xerogel) and its evolution depend strongly on the processing conditions. The gel powders were heated in open air for more than 10 h at fixed temperatures ranging from 125 to 1400° C, with hold at 300° C and 500° C for 0.5 to 1 h.

2.2. Thermal analysis

Differential thermal analysis (DTA) and thermogravimetry (TG) were carried out for identification and characterization. The xerogel exhibited two endothermic peaks at ~ 120 and 475° C and an exothermic peak at 1200° C. The weight loss was 19%, comparable to that expected from the reaction,

$$2\text{AlOOH} \rightarrow \text{Al}_2\text{O}_3 + \text{H}_2\text{O} \quad (1)$$

By observing the DTA in the samples heated at 125° C, 350° C and 900° C we could identify the first endo peak to the expellation of water and the second to the conversion into the γ phase.

2.3. Infrared absorption

The free water molecules and hydroxyl groups have characteristic vibration frequencies which absorb energy in the IR region. In boehmite doublets are expected at 3297 cm^{-1}, 3090 cm^{-1} corresponding to stretching mode of AlO–H and at 1080 cm^{-1}, 1160 cm^{-1} corresponding to Al–OH bending mode [3]. The free water is identified by the absorption at 1630 cm^{-1}, corresponding to H–O–H bend. The heat-treated gel powders were dispersed in KBr pellets and the IR absorption was measured in the range, 2 to 2.5 μm. The results are shown in Fig. 1. We observe unresolved doublets at 3300 cm^{-1}, 3090 cm^{-1} and 1155 cm^{-1}, 1070 cm^{-1} corresponding to boehmite. The other peaks in this spectrum are at,

3480 cm^{-1} H–OH stretch
1630 cm^{-1} H–O–H bend
2100 cm^{-1} hydrogen bonded OH

The broad band in the region 1000 to 400 cm^{-1} corresponds to Al–O vibrational modes.

Following the dehydration sequence with thermal treatment, from Fig. 1, we can infer that, at 350° C, the boehmite gel transists to the γ-phase. The characteristic doublets are no longer present. The free water modes at ~3500 cm^{-1} and ~1630 cm^{-1} are present. These are due to the adsorbed water in the heat-treated powder. Because of the porous nature, this material has a great tendency to absorb water. This was corroborated by the DTA measurements of the heat treated samples. The IR spectrum is identical to Fig. 1b for powders heat treated between 350 and 800° C. The free water peaks became negligible in the δ-phase, (Fig. 1c), for samples at 900° C and 950° C, and at 1200° C or above IR spectra were similar to α-Al$_2$O$_3$.

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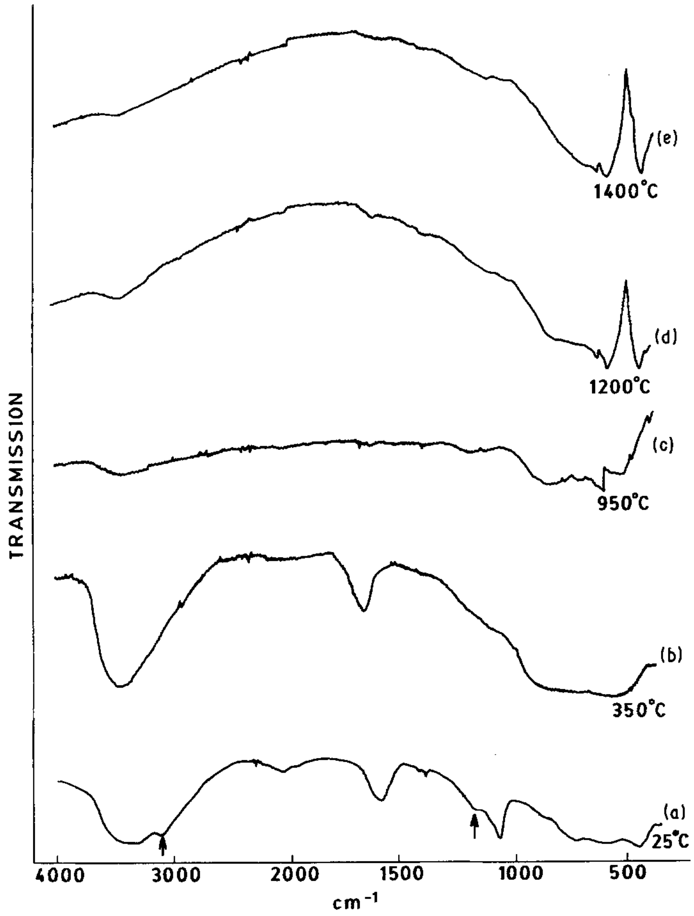


Figure 1 Infrared absorption in the gel powders: (a) boehmite, (b) γ-alumina, (c) δ-alumina (d) α-alumina. (e) α-alumina arrows denote the shoulder of the doublet.

2.4. Microstructure

A selected area diffraction (SAD) of a thin film of carbon coated gel showed diffuse rings and spots, and the microstructure revealed pore spacings ~ 8 nm (Fig. 2), indicating fine size and poor crystallinity in the material. The scanning electron micrographs (SEM) of the transparent gel glasses were often featureless like any glass.

The glasses were prepared by evaporating the gel in a petri dish. The vertical shrinking was much larger than the radial. This directional dehydration affects the microstructure as seen from the optical micrograph of Fig. 3. Doping with copper powder in trace quantity brought out the polymeric nature prominently in the microstructure. The amount of copper added was very small and with a wavelength dispersion analyser we found this to be less than the background count. We also found the material to be pure and devoid of impurities like silicon, calcium, chlorine, magnesium and iron by scanning at their wavelengths. But the aluminium percentage was different for the spot and area analyses. We are not sure whether it is due to porosity in the material or due to density fluctuations.

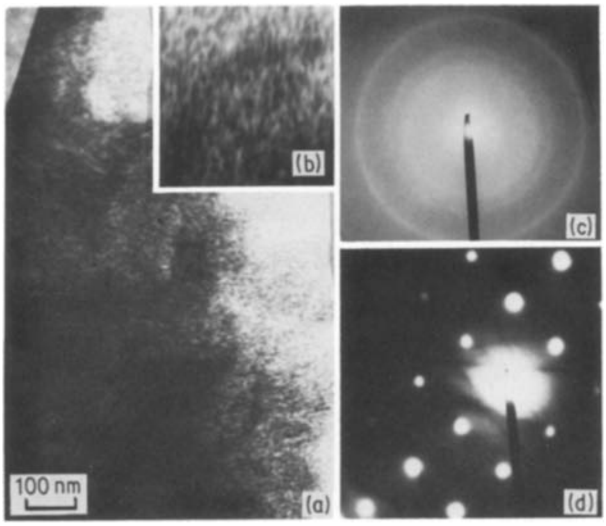


Figure 2 Boehmite gel film — transmission electron micrographs showing (a) lamellar porous microstructure, (b) magnified three times at a selected spot in a, (c) and (d) selected area diffractions.

The fractured surface in all the glass samples, heated or otherwise, had a layered texture. Thermal gradients associated with dehydration in a shallow dish accounts for this microstructure and partial orientation of the crystalline lamellae. Such a behaviour is observed in a polymer frozen in a mould [4]. The transparent gel glass becomes opaque when heated at 1000° C for 10 h. The microstructure consists of uniformly distributed black patches as in Fig. 4. We think this could be due to the appearance of the θ-phase because the XRD in this sample indicated more lines, than those expected of the δ-phase. These lines were absent in the powder sample heated at 1000° C. It was noted that the exposure to electron irradiation while scanning darkened these areas in the gel glass.

Experiments are being carried out to understand the sintering behaviour of the gel material. A preliminary result shows that the gel alumina pellet prepared out of a powder calcined at 1000° C for 10 h (δ-alumina) had low density (~ 80%) compared to the pellet of α-alumina (95%) prepared under identical conditions.

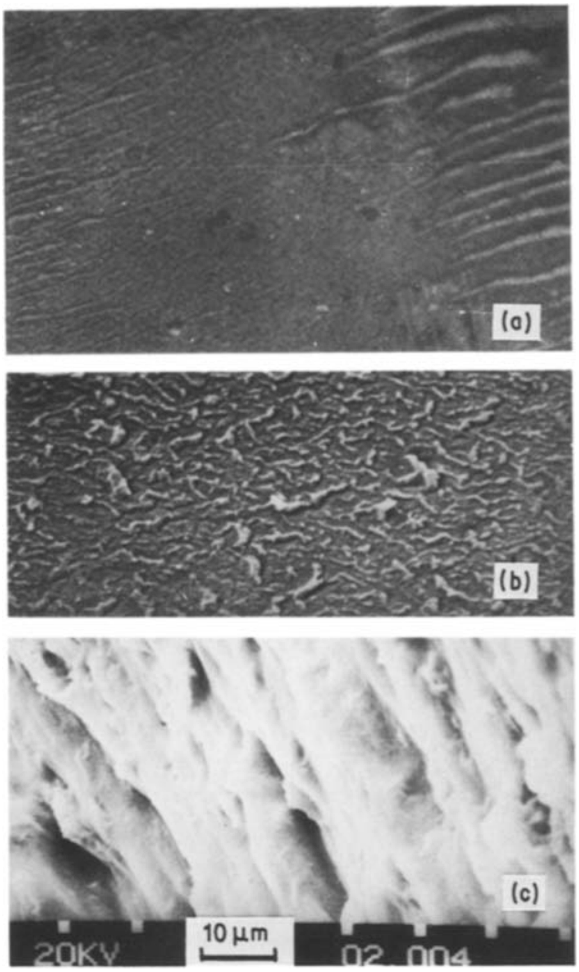


Figure 3 Boehmite glass (a) optical micrograph, (b) electron micrograph of a copper doped gel, (c) fractured surface of (b).

The sintering was done in air at 1500° C for 70 h. The fractured surface of the α-alumina pellet showed well faceted grains of average size $\sim 15\,\mu$m whereas the gel pellet had elongated grains of length 6 μm with 1.5 μm diameter (Fig. 5). This we think is due to the polymeric nature of the δ-phase resulting in particles of different morphology, even after attaining the crystalline α-phase.

2.5. X-ray diffraction

We heat-treated the gel powders at fixed temperatures for more than 10 h and recorded the diffraction at room temperature. Depending on the heating temperature, an equilibrium phase is attained. A Philips spectrometer with a Debye-Scherrer camera of 57.34 mm diameter was used with Cu$K\alpha$ ($\lambda = 0.154$ nm) and Mo$K\alpha$ ($\lambda = 0.711$ nm) radiations. As the diffraction rings were broad and diffuse, they were classified as weak, medium, strong and intense. To resolve the doublets, if any, a Philips powder diffractometer was also used. We found that in the γ-phase the doublets expected according to Lippen's [5] classification were broad lines and could not be resolved precisely. The line broadening gave a size estimate of 30 nm, too coarse compared to TEM estimate of 8 nm. The diffraction patterns taken for several heated materials, both powder and glass, could be classified in the known phases [5, 6] and are shown in Fig. 6. The gel glass differed from the powder only in the δ-phase pattern. At 1000° C the gel glass was found to contain a mixture of θ-phase along with δ-phase.

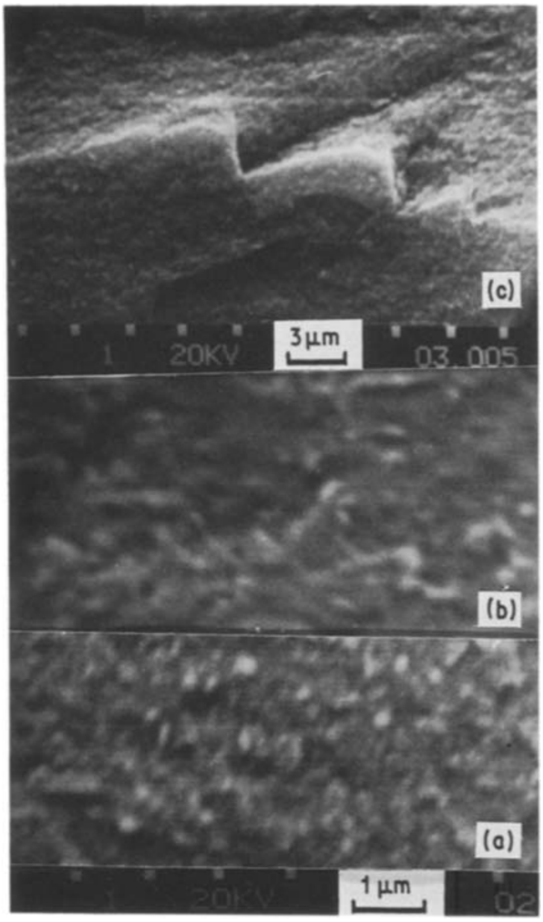


Figure 4 (a) boehmite glass, (b) heated at 600° C for 10 h, (c) fractured surface.

As γ-phase had few rings with the Cu$K\alpha$ radiation it was difficult to index them unambiguously. Moreover, there is ambiguity [6, 7] and some lack of clarity in the classification of the structure of this phase. With Mo$K\alpha$ radiation, more lines were obtained. This has helped us in resolving the structure of this phase. The results of the indexing are given in the Tables I, II and III for the boehmite, γ-phase and δ-phase respectively. They are compared with Lippen's [5] measurements

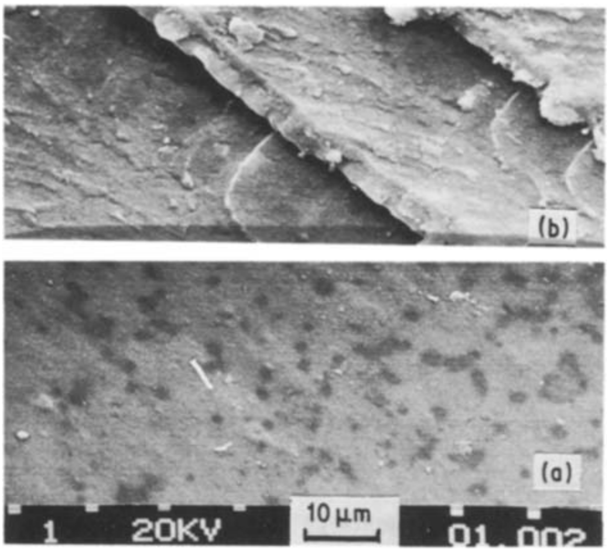


Figure 5 (a) Gel glass heated to 1000° C (b) fractured surface in (a).

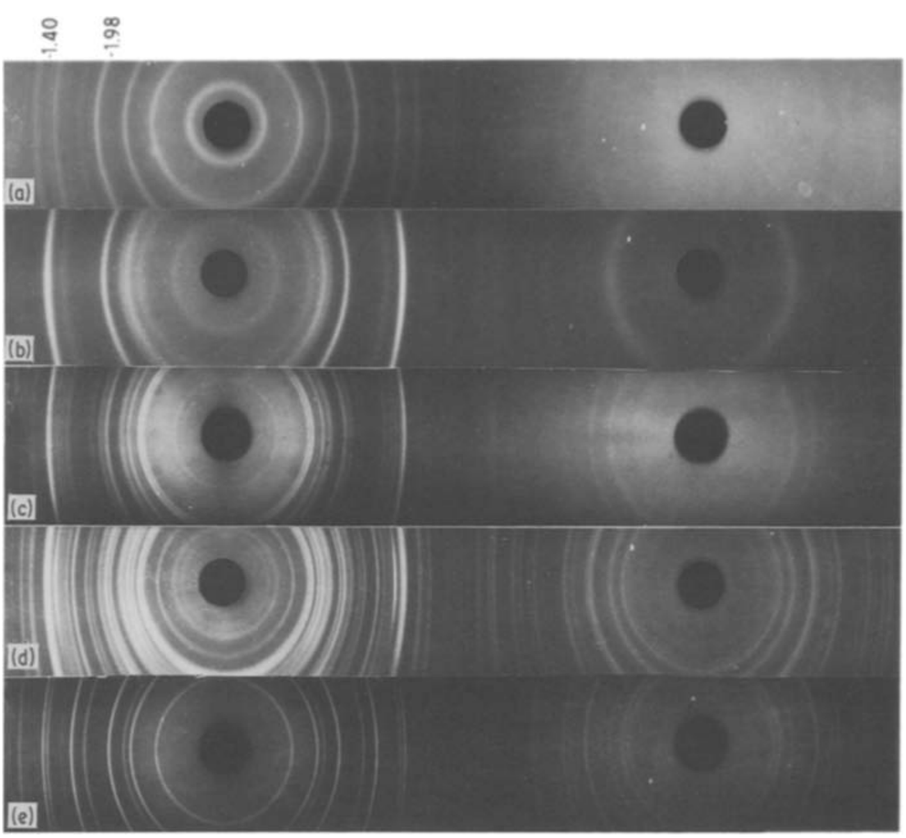


Figure 6 X-ray powder diffraction in (a) boehmite powder, (b) boehmite powder heated at 600° C for 10 h (γ), (c) boehmite powder heated at 1000° C for 10 h (δ), (d) boehmite gel glass heated at 1000° C for 10 h (δ), (e) boehmite powder heated at 1200° C for 10 h (α).

and there is general agreement. The lattice parameters calculated from a few *d*-spacings were refined using Nelson–Riley extrapolation functions [8]. The extrapolation functions are used to minimise errors in θ or d arising from experimental factors like film shrinkage and off-centering of the specimen. The *d*-spacings, calculated from these, are compared with our observed values.

3. Discussion

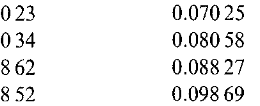
3.1. Boehmite

The starting material, boehmite gel was aluminium oxyhydroxide, in a transparent glass form or as a dry powder. The glass was highly porous (~60%) and partially crystalline as the diffuse, broad rings suggest. Yoldas [1] found that the scattering from these fine particles could be interpreted in terms of a Debye model for scattering from a coiled chain, of length $R \simeq 31$ nm. We have evidence of this polymeric nature from the microstructure shown in Fig. 2. A network polymer is non crystalline with certain coherent regions of crystallinity, the relative amount of which depends on the processing conditions. Leonard *et al.* [9] considered the amorphous nature of alumina and calculated the radial electron density distributions, to compare with their X-ray diffraction observations.

TABLE I X-ray diffraction in boehmite with Mo$K\alpha$ radiation

I	d_{observed} (nm)	$d_{\text{calc.}}$ (nm)	*hkl*
w	0.113 25	0.113 23	2 2 0
m	0.131 29	0.131 29	1 2 5
w	0.140 49	0.139 66	2 0 2
m	0.145 12	0.145 16	1 2 3
w	0.166 61	0.166 67	1 1 5
s	0.186 81	0.186 80	1 0 5
s	0.236 37	0.236 36	0 1 4
s	0.317 47	0.316 54	0 1 2
s	0.639	0.615 45	0 0 2

Lippens and Wilson [5, 7] studied micro crystallites of boehmite using electron diffraction and X-rays. The electron diffraction spots for boehmite, γ and δ-phases were found to exhibit streaking effects indicative of disorder in the structure. Boehmite is isomorphous to FeOOH. Each metal atom is surrounded by a distorted octahedron of oxygen atoms. The $Al-O_6$ octahedra chains are joined to form an interlocking double molecular layer of the form,



$$[\mathrm{HO{-}Al}\langle^{\mathrm{O}}_{\mathrm{O}}\rangle\mathrm{Al{-}OH}]_n \qquad (2)$$

The zigzag chains are parallel, forming layers with OH

TABLE II X-ray diffraction in γ-alumina with Mo$K\alpha$ radiation and Cu$K\alpha$ radiation

I	d_{observed} (nm)	$d_{\text{calc.}}$* (nm)	*hkl*
w	0.070 23	0.070 25	8 8 0
m	0.080 34	0.080 58	8 4 4
w	0.088 62	0.088 27	8 4 0
w	0.098 52	0.098 69	8 0 0
w	0.102 7	0.102 78	7 3 1/5 5 3
m	0.114 0	0.113 95	4 4 4
w	0.121 66	0.121 40	5 3 3†
i	0.140 30	0.139 57	4 4 0
m	0.152 73	0.151 94	5 1 1/3 3 3
I	0.198 63	0.197 37	4 0 0
m	0.229 14	0.227 91	2 2 2
s	0.240 69	0.238 94	3 1 1
m	0.280 1	0.279 13	2 2 0
m	0.456 1	0.455 82	1 1 1

*System cubic, $a = 0.7895$ nm.
†The indexing below this line is from Cu$K\alpha$ radiation. All indicii are in agreement with Lippens.

TABLE III X-ray diffraction in δ-alumina

I	d_{observed} (nm)	$d_{\text{calc.}}$ (nm)	*h k l*
w	0.079 95	0.079 96	7 7 2
w	0.080 64	0.080 67	7 7 0
w	0.081 71	0.081 71	5 8 7
w	0.085 35	0.085 31	6 7 4
m	0.099 70	0.099 63	7 3 7/5 6 4
m	0.300 8	0.129 89	6 1 2/4 4 7
I	0.139 54	0.139 53	4 4 0*
w	0.147 88	0.147 91	5 1 5
w	0.154 3	0.154 54	5 1 3
w	0.181 42	0.180 65	3 1 9
m	0.194 53	0.192 82	4 1 0
m	0.202 71	0.198 75	4 0 0
m	0.228 02	0.227 95	2 2 6
m	0.245 75	0.245 78	3 1 2
s	0.274 14	0.273 25	2 2 2
m	0.287 75	0.288 16	1 1 7

*Below this reflections have been indexed by Lippens and are in agreement with ours.

groups outside. The layers are linked by hydrogen bonds of length about 0.270 nm. The crystalline boehmite has an orthorhombic unit cell with axes $a = 0.2861$ nm, $b = 0.3696$ nm, $c = 1.2233$ nm [5]. The gel is probably pseudoboehmite which is similar in diffraction pattern [3] but because it contains more water, the spacings of the 0 0 2 reflections are shifted. We found the spacing for this reflection as ~ 0.64 nm whereas a crystalline boehmite has $d = 0.611$ nm. A freshly prepared pseudoboehmite with 1.7 moles of water has $d = 0.67$ nm. The extra interlamellar water also extends the lattice in an irregular way. Our results shown in Table I are in good agreement with the calculated values obtained from the lattice parameters as, $a = 0.2861$ nm, $b = 0.3691$ nm and $c = 1.2309$ nm which are quite close to the expected values.

The dehydration sequence, deduced from XRD and IR was,

$$\text{AlOOH} \xrightarrow{T\gamma} \gamma\text{-Al}_2\text{O}_3 \xrightarrow{T\delta} \delta\text{-Al}_2\text{O}_3 \xrightarrow{T\theta} \theta\text{-Al}_2\text{O}_3 \xrightarrow{T\alpha} \alpha\text{Al}_2\text{O}_3 \qquad (3)$$

Where $T\gamma$, the transition temperature to γ-phase was between 300 and 350° C, $T_\delta \rightarrow 800$ to 900° C, $T_\theta \rightarrow$ 1000 and 1200° C and $T_\alpha \rightarrow \geqslant 1200$° C.

We found the phases to be very stable and did not change with time e.g. gel sample heated at 950° C for 10 h and 900° C for 7 days had the same δ-phase, sample heated at 350° C for 10 h and 800° C for 10 h had the same γ-phase without admixture of other phases.

3.2. γ-alumina

This is a porous, reactive material with large surface area and used widely as a catalyst. It is prevalent over a longer range of treatment temperatures, 350 to 800° C, compared to other phases. The dehydration of boehmite to γ-Al_2O_3 is viewed as following: The expellation of water by an internal condensation of protons and hydroxyl groups between the layers is accompanied by the collapse of the layer and a cubic structure is formed as a result of the rearrangement of oxygen atoms. The pseudomorphosis relations of boehmite and γ-alumina were considered similar to the transformation from γ-FeOOH to γ-Fe_2O_3 [5] and a spinel structure with tetragonal distortion was proposed by Lippens [5].

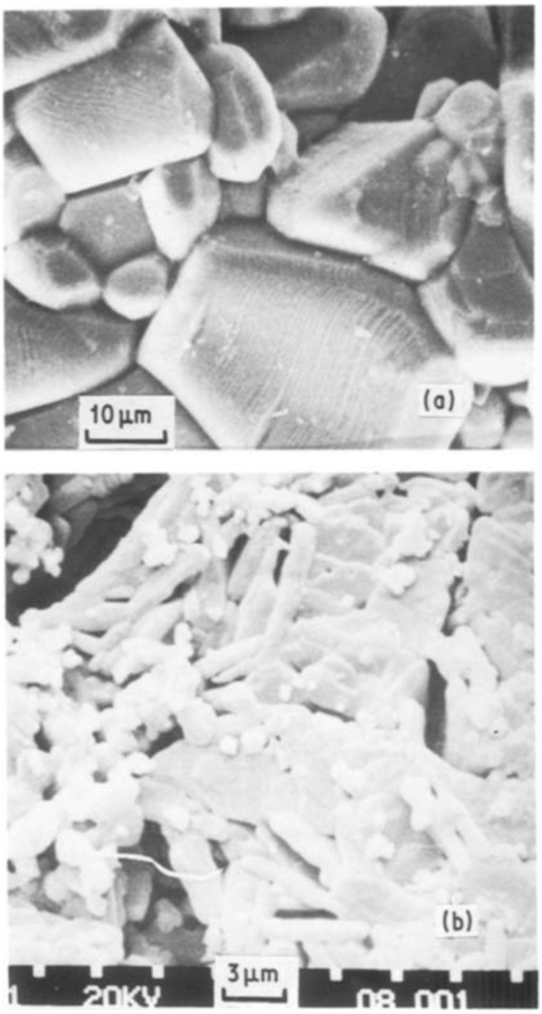


Figure 7 Grain morphology in the fractured surface of pellets sintered at 1500° C for 70 h (a) α-alumina (b) gel powder precalcined at 1000° C for 10 h.

Rooksby classified γ-phase as cubic with $a = 0.791$ nm [10]. Saalfeld [11] proposed a defect NaCl structure with tetragonal distortion and shortened c axis. Wilson [7] using electron diffraction and X-rays, proposed a diffusion mechanism of dehydration. He proposed a tetragonal structure with $a = 0.796$ nm and $c = 0.781$ nm. But he observed that with increase in time or temperature (> 400° C) of heat treatment, the degree of distortion decreases.

Our results are given in Table II. All the observed reflections with Cu$K\alpha$ were identical to Lippens and Rooksby's observations. The doublets at $d = 0.140$ and 0.198 nm were not resolved in the diffractometer recordings. The lines were broad. All the indices are allowed reflections for an f.c.c. lattice. Our calculated values for a cubic, $a = 0.7895$ nm were in good agreement with the observed. Lippens [5] had proposed a tetragonal structure with $a = c = 0.563$ nm and $b = 0.782$ nm.

It has been mentioned [3] that a small amount of water is necessary to stabilize the γ-Al_2O_3 and γ-Fe_2O_3 structures. It is proposed that water introduces protons into the octahedral vacancies in the spinel and gives a hydrated aluminium spinel of the form HAl_5O_8 or $Al_8(Al_{12}H_4)O_{32}$ with aluminium outside the parenthesis in the tetrahedral sites while inside the parenthesis, aluminium in octahedral holes. Spinel corresponds to a composition γ-$Al_2O_3 \cdot 1/5H_2O$ and loses its last trace of water $\geqslant 1000°$ C. Since we have an IR spectrum with free water present in the γ-phase, the distortion is probably removed. We like to mention here that γ-Fe_2O_3 structure has been reported recently [12]. Using a convergent beam electron diffraction, a primitive cubic lattice with $a = 2.5$ nm has been suggested. Under an electron beam, order/disorder type transition takes place with gradual change of lattice parameter to 0.833 nm.

Since some of the reflections are also common to the δ-phase, we found that by taking these (namely 4 4 0, 4 0 0, 3 1 1) for calculating the parameters, we get $a = b = 0.794$ nm and $c = 2.35$ nm, similar to the δ-structure. Hence in the literature we find discrepancy in the identification of γ and δ-phases.

3.3. δ-phase

Our results are as shown in Table III and agree with Lippens. The unit cell is tetragonal with parameters $a = b = 0.794$ nm and $c = 2.35$ nm. We found from the microstructure and XRD that in the gel glass, there is probably a mixture of θ-phase and this was absent in the powder. We attribute this to the directed shrinking which takes place in a petri dish. This might affect the arrangement of oxygen atoms, owing to the texture introduced and manifest dominantly at a high temperature.

3.4. α-phase

The hexagonal α-phase evolves in the powder at a temperature above 1200° C. All measurements namely IR (Al–O bands), sharp lines in XRD and DTA peak, support the crystalline order in this phase. Our indices and parameters agreed with corundum structure. But in the sintered pellets, prepared at 1500° C with heating for 70 h, the fractured surface reveals the importance of morphology and its retention. Whereas α-alumina pellets had faceted grains, the gel powder, though attaining the α-phase, had elongated grains along with the spherical (Fig. 5). This we trace to the polymeric nature of the boehmite gel and the δ-phase. Some of the features noted in these preliminary results on sintering were:

(a) Low density for the gel powder, which did not improve by increasing the duration of heating.

(b) Smaller grains for the gel powder

3.5. Optical properties

The disorder that was noticed in the XRD and microstructure of boehmite gel, γ and δ-alumina is well supported by the transmission properties in the visible range and near infra (0.2 to 2.6 μm wavelength range). In spite of the large porosity ($\sim 60\%$) the gel-glass was transparent, because of the disorder and the fine size the pores and particles. The opacity, which set in at 1000° C and presence of monoclinic phase marks probably the beginning of crystalline long range order in the process of dehydration.

4. Conclusion

From our results we conclude that,

(a) the polymeric partially crystalline, boehmite gel evolves to ordered crystalline, α-alumina phase, on thermal treatment;

(b) the transition phases γ and δ are partially disordered and probably are polymeric;

(c) the morphology namely fine size and polymeric nature of the gel is reflected in the grains of the sintered gel powder pellet;

(d) the evolution of order is reflected in the microstructure and optical properties of the gel materials.

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