# Self-controlled growth in highly stable $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles in mesoporous structure

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Highly stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles are obtained in a mesoporous structure (10–25% porosity) by reconstructive decomposition of a mesoporous AlO(OH) *x* H<sub>2</sub>O, *x* ~ 0.7, powder followed by annealing at 1475–1900 K. At *x* ~ 0.7, self-controlled AlO(OH) *x* H<sub>2</sub>O  $\rightarrow$  Al<sub>2</sub>O<sub>3</sub> molecular decomposition occurs in a controlled desorption of H<sub>2</sub>O through pores at 330–650 K. It was achieved by a novel hydrolysis method of Al metal with nascent surfaces in water at 295 K. Average  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystallite size hardly grows to 30–50 nm (several hundred nanometers otherwise in a bulk sample) at 1475–1900 K. They are arranged through pores in a specific fashion as observed in TEM micrographs. A network structure forms of surface atoms in high-energy crystallites in a high configurational entropy (governs improved stability and superplasticity or other properties) by minimizing the Gibbs free energy. A metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase exists in processing at low temperature such as 1475 K. It has a modified X-ray diffraction or IR spectrum of equilibrium phase after annealing (reorders interstitial vacancies) at 1525 K or higher temperatures. It is proposed that a mobile Al<sup>3+</sup> hole in a site neighboring an AlO<sub>6-δ</sub> architect defect creates a center to a plane slipping or twin structure formation. Mesopores provide sites for crack initiation and also for crack arrest in confined cracks (support a high failure strain).

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# 1 Introduction

Mesoporous materials, which comprise nanoparticles distributed through pores of 2-50 nm diameter in a specific structure, have been the subject of considerable interest owing to their potential applications in catalysts, hot filters, adsorption media, phosphors, and microelectronics [1-7]. Thermal stability with a controlled microstructure at this scale is one of the most important parameters of the material of reproducible properties. It determines the activity and performance of the material in a specific device as per its chemistry and other properties. A large surface area, pore structure, and surface chemistry play an essential role especially in adsorption and catalysis.

In this series, alumina (Al<sub>2</sub>O<sub>3</sub>) is a paradigm for fabricating mesoporous or classical ceramics [2–4]. Doping with a foreign metal oxide refines a stable microstructure and improves or adds other useful properties. Zhang et al. [4] stabilized a mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 1–5 mol% Ce<sup>3+</sup> or La<sup>3+</sup>. A composite mesoporous structure allows Al<sub>2</sub>O<sub>3</sub> molecules access to large internal surfaces and cavities that enhance their catalytic and adsorption activities. Nanocrystals of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are widely used as adsorbents, catalysts or catalyst carriers, gas sensors, coating and soft abrasives because of fine size, high surface area, and catalytic activity of their surfaces. These remarkable properties have a great deal of interest in understanding their origin and mechanisms in nanostructures [8–15].

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 $\gamma$ -Al<sub>2</sub>O<sub>3</sub> has a lower surface energy,  $\sigma = 0.79 \text{ J/m}^2$ , than  $\sigma = 2.04 \text{ J/m}^2$  in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and becomes energetically stable at surface area  $A \ge 125 \text{ m}^2/\text{g}$ , i.e.  $d \le 13 \text{ nm}$  diameter in a spherical crystallite, and thermodynamically stable at even smaller  $A \sim 75 \text{ m}^2/\text{g}$  at 800 K [11].  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> can maintain  $A \sim 150 \text{ m}^2/\text{g}$  at 1073 K while  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> coarsens at  $A \le 50 \text{ m}^2/\text{g}$  at such temperatures.  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, supposed to have an intermediate  $\sigma$  value, appears at intermediate A in coarse to  $\gamma \rightarrow \alpha$  transformation [14]. Molecular dynamics simulations [16], assuming preferential exposure of the surfaces with lowest energy, predicts  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as the energetically stable phase as A exceeds 125 m<sup>2</sup>/g. Distribution of Al<sup>3+</sup> and vacancies in tetrahedral and octahedral sites in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [17] has a larger entropy S than in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> which has only octahedral sites [17, 18]. The  $\gamma \rightarrow \alpha$  transition has as large change in S as 5.7 J/K mol [11], demonstrating  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to be the probable phase to exist in small particles,  $A \ge 100 \text{ m}^2/\text{g}$ , at room temperature.

In this paper, we report the synthesis of monolithic  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in a self-confined 30–50 nm dimension through pores in a mesoporous structure. Firmly stable particles form at a temperature as low as 1475 K and do not grow much on raising the temperature as high as 1900 K. Pores support a metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> structure. The equilibrium  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> structure occurs by a local atomic reordering at 1525 K or higher temperature. The results are analyzed and modeled with X-ray diffraction, microstructure, and vibrational spectrum. A twin boundary structure has been seen earlier in high-resolution electron microscopic (HREM) images in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [18–20]. It influences grain growth, thermal stability, and other macroscopic properties. Small levels of porosity  $\Phi$  (5–10%) offer superplasticity [10]. Uniformly distributed pores provide sites for both crack initiation and crack arrest, leading to a large number of short cracks, and to higher failure strains.

# 2 Experiment details

A mesoporous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> structure is derived from a mesoporous AlO(OH) *x* H<sub>2</sub>O, *x* ~ 0.7, precursor with  $\Phi = 18\%$  and d = 30 nm average crystallite size. As described earlier [15], it has been synthesized by a novel hydrolysis method of a high-purity (99.9%) Al metal (in the shape of a thin plate) with nascent surface in distilled water at 295 K. A self-induced exothermic hydrolysis reaction, Al + 2H<sub>2</sub>O  $\rightarrow$  AlO(OH) +  $\frac{3}{2}$  H<sub>2</sub>, occurs as soon as the Al metal is immersed in water. The resulting AlO(OH) instantaneously reacts with H<sub>2</sub>O and converts to AlO(OH) *x* H<sub>2</sub>O. This is filtered and dried to a powder at room temperature in air. In sol-gel or other wet methods, a metastable AlO(OH) *x* H<sub>2</sub>O precursor appears in a gel with a larger  $x \ge 1.0$  [21, 22]. A refined mesoporous Al<sub>2</sub>O<sub>3</sub> powder ( $\Phi = 45\%$ ) appears on dehydration and reconstructive thermal decomposition at 500–600 K. It transforms to a mesoporous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at temperature as low as 1475 K (Table 1).

The phase analysis was carried out with X-ray diffraction of annealed samples at elevated temperatures, using a P.W. 1710 X-ray diffractometer with filtered Co K<sub> $\alpha$ </sub> radiation of  $\lambda = 0.17902$  nm wavelength. Their microstructures were studied with a transmission electron microscope (TEM), model-JEM 2000 CX, in conjunction with an energy-dispersive X-ray spectrum analyzer for in-situ elemental analy-

trade name	density <sup>a</sup> (g/cm <sup>3</sup> )	porosity (%)	V (nm <sup>3</sup> )	$A (10^3 \text{ m}^2/\text{g})$	$S_{g}^{b}$ (m <sup>2</sup> /g)		
Boehmite	1.85 (2.25)	18	0.429	3.70	108.1		
$\theta$ -Al <sub>2</sub> O <sub>3</sub>	2.50 (3.58)	30	0.186	3.38	200.0		
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	2.98 (3.98)	25	0.770	4.84	57.5		
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	3.20 (3.98)	20	0.767	4.82	48.1		
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	3.25 (3.98)	18	0.755	4.77	45.0		
$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	3.60 (3.98)	10	0.763	4.80	33.3		
	trade name Boehmite $\theta$ -Al <sub>2</sub> O <sub>3</sub> $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	$\begin{array}{c} \text{trade name} & \text{density}^{a} \\ \hline \text{(g/cm}^{3)} \\ \hline \text{Boehmite} & 1.85 (2.25) \\ \theta \text{-Al}_{2}\text{O}_{3} & 2.50 (3.58) \\ \alpha \text{-Al}_{2}\text{O}_{3} & 2.98 (3.98) \\ \alpha \text{-Al}_{2}\text{O}_{3} & 3.20 (3.98) \\ \alpha \text{-Al}_{2}\text{O}_{3} & 3.25 (3.98) \\ \alpha \text{-Al}_{2}\text{O}_{3} & 3.60 (3.98) \\ \end{array}$	$\begin{array}{c c} trade name & density^{a} & porosity \\ (g/cm^{3}) & (\%) \\ \hline \\ Boehmite & 1.85 (2.25) & 18 \\ \theta-Al_{2}O_{3} & 2.50 (3.58) & 30 \\ \alpha-Al_{2}O_{3} & 2.98 (3.98) & 25 \\ \alpha-Al_{2}O_{3} & 3.20 (3.98) & 20 \\ \alpha-Al_{2}O_{3} & 3.25 (3.98) & 18 \\ \alpha-Al_{2}O_{3} & 3.60 (3.98) & 10 \\ \hline \end{array}$	trade namedensity <sup>a</sup> (g/cm <sup>3</sup> )porosity (%)V (nm <sup>3</sup> )Boehmite $1.85 (2.25)$ $18$ $0.429$ $0-Al_2O_3$ $0-Al_2O_3$ $2.50 (3.58)$ $30$ $0.186$ $\alpha-Al_2O_3$ $\alpha-Al_2O_3$ $2.98 (3.98)$ $25$ $0.770$ $\alpha-Al_2O_3$ $\alpha-Al_2O_3$ $3.20 (3.98)$ $20$ $0.767$ $\alpha-Al_2O_3$ $\alpha-Al_2O_3$ $3.25 (3.98)$ $18$ $0.755$ $\alpha-Al_2O_3$ $\alpha-Al_2O_3$ $3.60 (3.98)$ $10$ $0.763$	trade namedensitya (g/cm3)porosity (%)V (nm3)A (103 m2/g)Boehmite1.85 (2.25)180.4293.70 $\theta$ -Al_2O_32.50 (3.58)300.1863.38 $\alpha$ -Al_2O_32.98 (3.98)250.7704.84 $\alpha$ -Al_2O_33.20 (3.98)200.7674.82 $\alpha$ -Al_2O_33.25 (3.98)180.7554.77 $\alpha$ -Al_2O_33.60 (3.98)100.7634.80		

**Table 1** Density, porosity (%), lattice volume (*V*), lattice surface area (*A*), and specific particle surface area ( $S_g$ ) in AlO(OH) *x* H<sub>2</sub>O,  $\theta$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> powders.

<sup>a</sup> The density calculated from V is given in parentheses.

<sup>b</sup> The  $S_{g}$  value refers to spherical shape of particles of average size *d* as determined by the  $\Delta 2\theta_{1/2}$  value.

sis. No impurity has been found in a detectable 0.1 at.% or still lower trace. Average *d*-value has been calculated from the widths  $\Delta 2\theta_{1/2}$  of the X-ray diffraction peaks with the Debye–Scherrer relation. Mesoporous structure of the sample was studied by  $\Phi$  value, obtained from the difference in observed and theoretical values of its density and by the standard N<sub>2</sub> gas sorption method at low temperature such as 77 K. The density was measured, within an error of ±0.01 g/cm<sup>3</sup>, by displacement of N<sub>2</sub> gas by Archimedes principle using a Penta Pyknometer (from Quanta Chrome, USA).

## **3** Results and discussion

#### 3.1 Molecular growth in mesoporous Al<sub>2</sub>O<sub>3</sub> structure

The hydrolysis of Al atoms by the reaction with  $H_2O$  molecules at the nascent Al plate surface (immersed in water) occurs in a controlled manner by adding the reaction species of  $OH^-$  ions in successive steps.  $H_2O$  molecules that come into contact with the Al surface instantaneously dissociate into  $H^+$  and  $OH^-$  ions to conduct the hydrolysis as in Fig. 1.

The intermediate  $[AlO(OH)]^{2+}$  or  $[AlO(OH)_2]^+$  reaction species in step (1a) or (1b) readily proceeds to the AlO(OH) molecule by neutralizing a total of zero electronic charge. It occurs by just releasing a proton H<sup>+</sup> with a minor redistribution of the internal energy. The energy, being a local property, readily redistributes by dissipation of the excess heat through the surroundings.

Two primary driving forces, (i) the initial chemical potential  $\mu_e$  between the reaction species and (ii) the flow of the reaction species, drive the nascent AlO(OH) molecules to grow in a common direction perpendicular to the reaction surface. A unidirectional polymeric structure results in molecules interconnecting one another in successive steps as long as it is not disrupted by local perturbations. This is satisfied in a controlled reaction at room temperature. A model structure of this is shown in Fig. 2a. As the temperature rises above room temperature, the interstitial H<sub>2</sub>O molecules locally desorb and the structure redistributes in a modified Al<sub>2</sub>O<sub>3</sub> x H<sub>2</sub>O structure with 2AlO(OH)  $\rightarrow$  H<sub>2</sub>O + Al<sub>2</sub>O<sub>3</sub> molecular decomposition (Fig. 2b).

From the TEM micrograph (Fig. 3a), a non-disrupted AlO(OH) x H<sub>2</sub>O growth appears to last over several molecules. It results in particles with  $D \sim 35$  nm diameter. The particles distribute through pores (with 2 to 5 nm distance between particles) which develop when the reaction is disrupted by the local temperature. Their elongated ellipsoidal shapes, with  $\phi \sim 1.8$  aspect ratio, are in accord with their growth in a directional Al hydrolysis. The corresponding electron diffraction pattern (Fig. 3b) has four rings at interplanar spacing  $d_{hkl}$  of 0.492, 0.320, 0.237 and 0.190 nm in comparison to the 0.4850, 0.3198, 0.2358 and 0.1872 nm values in (002), (112), (213) and (314) reflections in X-ray diffraction (Fig. 4a) with lattice parameters a = 0.866 nm, b = 0.506 nm, c = 0.983 nm and  $\beta = 94^{\circ}34'$  in  $C_{2h}^{5}$  monoclinic structure

$$nAI + nH_{2}O \longrightarrow \left[ \begin{array}{c} OH & OH & OH \\ ..., AI & AI & AI \\ AI & AI & AI \\ \end{array} \right]_{n}^{n+} + \frac{1}{2}nH_{2} \qquad (1a)$$

$$\left[ \begin{array}{c} OH & OH OH OHOH OH \\ ..., AI & AI & AI \\ \end{array} \right]_{n}^{n+} + \frac{1}{2}nH_{2} \qquad (1b)$$

$$\left[ \begin{array}{c} OH & O OH & O OH \\ ..., AI & AI & AI \\ \end{array} \right]_{n}^{n+} + \frac{1}{2}nH_{2} \qquad (1c)$$

**Fig. 1** A schematic representation of surface hydrolysis of Al metal with nascent surface in AlO(OH) *x* H<sub>2</sub>O in water. The initial chemical potential  $\mu_e$  lies perpendicular to the surface.



**Fig. 2** a) A model  $[AlO(OH) x H_2O]_n$ , n = 8, metalloceramic polymeric structure in association of molecules one after another in a) directional Al hydrolysis. b) A polymeric structure retained in a controlled Al<sub>2</sub>O<sub>3</sub> x H<sub>2</sub>O phase transformation. It has a lot ( $x \sim 1.4$ ) of H<sub>2</sub>O molecules (shown by the solid circles) with hydrogen bonding in a microporous structure.

[23]. An average d = 30 nm, estimated from  $\Delta 2\theta_{1/2}$  in the peaks, compares with the size of particles in TEM, characterizing them to be single crystallites.

The model [AlO(OH)  $x H_2O]_n$ , n = 8, structure (Fig. 2a) has plenty of H<sub>2</sub>O molecules, since  $x \sim 1.4$ . The real value of *n* is still larger, of the order of 10<sup>5</sup> in  $D \sim 35$  nm structure, as can be determined by n = V/v, with  $V = \frac{4}{3}\pi \left[\frac{1}{2}D\right]^3 (\phi)^{-2}$  its average volume and  $v = 5.4 \times 10^{-2}$  nm<sup>3</sup> the AlO(OH)  $x H_2O$  molecular volume. A similar structure can be designed by a local molecular decomposition of it to Al<sub>2</sub>O<sub>3</sub>. In Fig. 2b, it is shown with a change in Al<sup>3+</sup> coordination from three to four. The Al<sup>3+</sup> cations in AlO<sub>4</sub> sites, as in liquid Al<sub>2</sub>O<sub>3</sub> [17], involve an excess oxygen ( $\zeta$ ) in average Al<sub>2</sub>O<sub>3+ $\zeta$ </sub>  $x H_2O$  composition. At  $n \to \infty$ ,  $\zeta \sim 0.75$  in the absence of oxygen vacancies. On heating, the H<sub>2</sub>O molecules are liberated, mostly over 500–600 K, in a porous structure. A shown in Fig. 4b, a high-energy amorphous state exists before it transforms to polymorphic Al<sub>2</sub>O<sub>3</sub>. It is obtained at 600 K with an energized AlO(OH)  $x H_2O$  with  $\Phi$  as much as 30% by Al hydrolysis in H<sub>2</sub>O vapour at ~310 K.

Part of the H<sub>2</sub>O or oxygen in porous Al<sub>2</sub>O<sub>3</sub> x H<sub>2</sub>O in Fig. 2b is slowly liberated at temperature sufficient enough to reorder Al<sup>3+</sup> and O<sup>2-</sup> in Al<sub>2</sub>O<sub>3</sub> polymorphs. It occurs as early as at 800 K by forming fine pores between growing structures in stable particles. Those H<sub>2</sub>O confined in between particles of a few



Fig. 3 a) TEM micrograph and b) electron diffractogram in mesoporous AlO(OH) x H<sub>2</sub>O.



**Fig. 4** X-ray diffraction peaks in mesoporous AlO(OH) x H<sub>2</sub>O in  $C_{2h}^{5}$  monoclinic crystal structure (curve a) and amorphous Al<sub>2</sub>O<sub>3</sub> x H<sub>2</sub>O obtained from it at 600 K for 2 h (curve b). Curve (c) is a close-up of curve (b) indicating three halos at 21.0, 29.1, and 43.6 nm<sup>-1</sup> wavevectors.

nanometers become immobile and hinder the particles from recombining and growing any more. In this case, they merely extend in tightly curved layers by enclosing the pores so as to minimize the total surface and volume Gibbs free energy. This is consistent with TEM micrograph (Fig. 5a) in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> obtained by heating the precursor at 1475 K for 2 h. Thin platelet particles of 15–30 nm diameter appear with pores in acicular shapes of 10–15 nm lengths with  $\phi \sim 2$ . This is in a refined microstructure in the precursor in Fig. 3a. The corresponding electron diffraction pattern (Fig. 5b) has four rings at 0.258, 0.225, 0.160, or 0.128 nm in (104), (006), (116), or (208) reflections.

Yang et al. [2] developed a similar large-pore (up to 14 nm) mesoporous  $Al_2O_3$  using a metalloceramic gel with poly(alkylene oxide) block copolymer as a structure-directing agent in a solution with  $AlCl_3$ . In  $AlCl_3$ -polymer solution in ethanol,  $Al^{3+}$  cations hydrolyze and polymerize into a network in a transparent gel at 313 K. The organic component burns out in a mesoporous  $Al_2O_3$  powder if heating the



Fig. 5 a) TEM micrograph and b) electron diffractogram in mesoporous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (metastable) powder after annealing at 1475 K for 2 h. Two typical diffraction spots in a twin structure are marked by the lines.



Fig. 6 A model mesoporous structure with hexagons of AlO<sub>4</sub> structural units in Al<sub>2</sub>O<sub>3</sub>.

gel (dried) at 673 K. It consists of nanocrystallites within relatively thick amorphous walls of 3.5 nm thickness. An altogether different structure with amorphous pore walls appears in silica and derivatives through a surfactant templating [1, 2]. This approach applies with sporadic success to-non-silica oxides. As compared to both of them, our method with Al metal hydrolysis seems to be rather simple, economic, and versatile for a large-scale synthesis of mesoporous  $Al_2O_3$  and composites. It involves no other chemical to promote the hydrolysis carried out in an aqueous solution with common metal salts.

A schematic model of the kind of structure we envisage in mesoporous  $Al_2O_3$  in this example is shown in Fig. 6. It consists of discrete fragments rather than a single continuous layer as per the TEM images. Townsend et al. [24] modeled a continuous layer structure in mesoporous carbon in terms of carbon rings. Harris et al. [7] extended this model with pentagons and hexagons of carbon rings, which more closely ascribe the observed curved surfaces in discrete fragments in mesoporous carbon deduced by carbonization of sucrose. In our model, curved and closed structures in  $Al_2O_3$  result from molecular association of  $Al_2O_3$  in  $AlO_4$  structural units. A molecular structure of interconnected network is retained on the grain surface on recrystallizing it into  $Al_2O_3$  polymorphs.

### 3.2 Controlled phase transformation in mesoporous Al<sub>2</sub>O<sub>3</sub> structure

Mesoporous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has a significant variation in X-ray diffraction as processed at different temperatures in the 1475–1900 K range. Figure 7 compares diffractograms in the samples processed at (a) 1475 K and (b) 1525 K for 2 h. As assigned in Table 2, diffractogram (a) involves a total of 17 peaks (peak intensity  $I_p \ge 3$  units) in addition to those in the corundum structure [25] in diffractogram (b) or Table 3. They are relatively broad, according to d = 28 nm, at 0.4503, 0.3075, 0.2840, 0.2720, 0.2370, 0.2310, 0.2250, 0.2165, 0.2025, 0.1961, 0.1910, 0.1735, 0.1490, 0.1455, 0.1440, 0.1370 and 0.1285 nm. A similar series of peaks (Fig. 7c) lie in A2/M monoclinic  $\theta$ -Al<sub>2</sub>O<sub>3</sub> structure (processed at 1275 K in 2 h) of lattice parameters a = 0.5650 nm, b = 0.2900 nm, c = 1.1720 nm, and  $\beta = 104.5^{\circ}$  against the reported a = 0.570 nm, b = 0.290 nm, c = 1.180 nm, and  $\beta = 104.5^{\circ}$  values [25]. It has 12 major peaks of 0.2839, 0.2721, 0.2553, 0.2437, 0.2309, 0.2249, 0.2013, 0.1916, 0.1540, 0.1487, 01453, and 0.1388 nm in  $\langle d \rangle = 12$  nm. The peak at 0.1388 nm, instead of the 0.2720 nm in the above series, is the most intense peak of the diffractogram.

Adversely, the present peak series has a larger  $V_0 = 0.190 \text{ nm}^3$  lattice volume in  $\langle d \rangle = 28 \text{ nm}$  over  $V_0 = 0.186 \text{ nm}^3$  in the  $\theta$ -Al<sub>2</sub>O<sub>3</sub> in  $\langle d \rangle = 12 \text{ nm}$ , with a = 0.5720 nm, b = 0.2920 nm, c = 1.1750 nm, and



**Fig. 7** X-ray diffraction peaks in nanoparticles in metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (curve a), usual  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (curve b), and  $\theta$ -Al<sub>2</sub>O<sub>3</sub> (curve c) as annealed at 1475 K, 1525 K and 1275 K for 2 h, respectively.

 $\beta = 104.5^{\circ}$ .  $V_0$  usually expands in the size effects in nanoparticles below a critical  $d = d_c$ . This is demonstrated with a high-resolution X-ray diffractogram in (113) peak in the true corundum structure in Fig. 8. The peak regularly shifts to smaller  $d_{hkl}$  as d grows from 35 nm in (a) to 41 nm in (c). An increase in  $d_{hkl}$  is noticed in d above 41 nm as in (e) in sample processed at 1900 K for 2 h. Possibly, a local O<sup>2-</sup> redistribution occurs in regular AlO<sub>6</sub> sites if not achieved before. It is known that  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> forms via  $\theta$ -Al<sub>2</sub>O<sub>3</sub> as a precursor state. Al<sup>3+</sup> in  $\theta$ -Al<sub>2</sub>O<sub>3</sub> lies in AlO<sub>4</sub> and AlO<sub>6</sub> sites in a spinel structure with cation vacancies mostly in AlO<sub>6</sub> sites [13]. Part of these vacancies are retained in oxygen-deficient AlO<sub>6- $\delta$ </sub>,  $\delta \le 2$ , sites on the phase transformation in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at early temperatures.

A close-up of the X-ray diffraction reveals a trace of these peaks to be present on annealing at temperatures as high as 1900 K. For example, in Fig. 9, seven additional peaks lie in modified positions and intensities at 0.2810, 0.2293, 0.1957, 0.1919, 0.1765, 0.1335, and 0.1273 nm after 2 h of annealing at 1700 K. Redistribution of intensities in the peaks confirms reordering of atoms in the lattice. The most intense reflection thus appears in (104) peak on annealing at 1475 K (Fig. 7a) while in (113) peak at 1700 K (Fig. 9). They have the same intensity if annealing at 1525 K (Fig. 7b).

The obtained structure, which is stabilized with immobile pores, behaves as highly rigid and is nonreactive to its further growth at these temperatures. The pores maintain a strict control of grain growth and thus allow it in true nanocrystallites. Otherwise, at such high temperature, it rapidly grows to several hundred nanometers [11, 12, 26]. This is not feasible with a non-porous precursor in which the molecules adhere to one another by strong hydrogen bonding. They do not dehydrate in mesoporous structure. A seeding by 0.2–2 mol% additive of CuO, NiO, or MgO [10, 12] has been used to control submicrometer  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> size. Spray pyrolysis with Al<sup>3+</sup> chloride or nitrate [27] and glycothermal treatment of Al<sup>3+</sup> hydroxide [28] give a reasonably controlled  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> size. Nevertheless, it does not come down below 100 nm in any case.

Modified sol-gel and other new methods are being developed in order to control  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> size in small crystallites [29–31]. Lin et al. [30] used an emulsion of Al(OH)<sub>3</sub> gel in oleic acid to obtain  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by firing it at temperature as high as 1373 K. Carbon, which is liberated by the decomposition of oleic acid during the thermal process, prevents the growth of agglomerates in a sequence of phase formation of the

$d_{hkl}$ (nm)		Ι	h	k	l	
observed	calculated					
0.4503	0.4353	15	0	0	3 <sup>a</sup>	
0.3476	0.3488	69	0	1	2 <sup>b</sup>	
0.3075	0.3265	5	0	0	4	
0.2840	0.2995	45	1	0	3 <sup>a</sup>	
0.2720	0.2612	58	0	0	$5^{\rm a}$	
0.2550	0.2560	100	1	0	$4^{c}$	
0.2435	0.2383	54	1	1	$0^{\rm c}$	
0.2370	0.2344	43	1	1	1	
0.2310	0.2238	38	1	1	$2^{a}$	
0.2250	0.2177	25	0	0	6 <sup>a</sup>	
0.2165	0.2063	12	2	0	0	
0.2085	0.2090	90	1	1	3 <sup>b</sup>	
0.2025	0.2038	35	2	0	$1^{a}$	
0.1961	0.1967	4	2	0	2	
0.1910	0.1925	22	1	0	6 <sup>a</sup>	
0.1785	0.1744	9	0	2	$4^{c}$	
0.1735	0.1700	40	1	0	7	
0.1601	0.1607	65	1	1	6 <sup>b</sup>	
0.1545	0.1549	16	2	1	$1^{c}$	
0.1511	0.1518	9	0	1	$8^{b}$	
0.1490	0.1517	10	1	2	$2^{a}$	
0.1455	0.1497	17	2	0	6 <sup>a</sup>	
0.1440	0.1468	6	1	2	3 <sup>a</sup>	
0.1405	0.1407	43	1	2	4 <sup>b</sup>	
0.1385	0.1376	45	0	3	$0^{\rm c}$	
0.1370	0.1339	43	1	2	5	
0.1285	0.1280	7	2	0	8	
0.1240	0.1245	10	1	0	10 <sup>b</sup>	
0.1234	0.1239	6	1	1	9 <sup>b</sup>	
0.1190	0.1191	3	2	2	$0^{\mathrm{b}}$	

**Table 2** Interplanar spacing  $(d_{hkl})$  and relative intensities (*I*) in characteristic peaks in X-ray powder diffraction in metastable phase in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanocrystals.

The calculated  $d_{hd}$  are from the average lattice parameters a = 0.4765 nm and c = 1.3060 nm. The sample has been annealed at 1475 K for 2 h. The peaks that match with other phases are marked as <sup>a</sup> $\theta$ -Al<sub>2</sub>O<sub>3</sub>, <sup>b</sup> $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and <sup>c</sup> $\theta$ -Al<sub>2</sub>O<sub>3</sub>, and <sup>c</sup> $\theta$ -Al<sub>2</sub>O<sub>3</sub>.

emulsion  $\rightarrow \gamma$ -Al<sub>2</sub>O<sub>3</sub>  $\rightarrow \delta$ -Al<sub>2</sub>O<sub>3</sub>  $\rightarrow \theta$ -Al<sub>2</sub>O<sub>3</sub>  $\rightarrow \alpha$ -Al<sub>2</sub>O<sub>3</sub>. Average *d*-value has been controlled to be 60 nm. No  $\delta$ -Al<sub>2</sub>O<sub>3</sub> phase appears in processing by a mesoporous boehmite precursor in our work. It is more effective in controlling grain growth in extremely small Al<sub>2</sub>O<sub>3</sub> crystallites of size under 50 nm at temperatures as high as 1900 K.

## 3.3 Critical dimension of thermodynamic stability in $\theta$ -Al<sub>2</sub>O<sub>3</sub> particles

The metastable  $\theta$ -Al<sub>2</sub>O<sub>3</sub> forms and exists in self-confined dimension,  $d \le R_c$ , as per its total surface and volume Gibbs free energies. To determine the critical value  $R_c$  of its thermodynamic stability, we studied  $\theta$ -Al<sub>2</sub>O<sub>3</sub> growth by heating at selected temperatures from 1100 to 1400 K for 2 h. As derived by  $\Delta 2\theta_{1/2}$ , it appears at  $d \sim 10$  nm and grows up to 20 nm.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> lies at  $d \le 10$  nm. The BET measurements give

$\mathbf{d}_{hkl} (\mathbf{nm})$		Ι	h	k	l	
observed	calculated					
0.3475	0.3484	76	0	1	2	
0.2550	0.2555	100	1	0	4	
0.2380	0.2381	44	1	1	0	
0.2085	0.2087	100	1	1	3	
0.1741	0.1742	42	0	2	4	
0.1603	0.1604	77	1	1	6	
0.1549	0.1548	2	2	1	1	
0.1515	0.1514	6	0	1	8	
0.1406	0.1406	31	1	2	4	
0.1375	0.1375	45	0	3	0	
0.1243	0.1242	12	1	0	10	
0.1236	0.1236	8	1	1	9	
0.1191	0.1191	4	2	2	0	
0.1187	0.1186	2	2	2	1	

**Table 3** Interplanar spacing  $(d_{hkl})$  and relative intensities (*I*) in characteristic peaks in X-ray powder diffraction in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanocrystals.

The calculated  $d_{\text{\tiny hill}}$  are from the average lattice parameters a = 0.4762 nm and c = 1.3020 nm. The sample has been annealed at 1525 K for 2 h.

10–25 nm average particle surface area diameter, with a volume to surface shape factor of 6. It converts to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> by a sudden increase in *d* of 35 nm on raising the temperature to 1475 K. A similar *d*-value has been reported by Wen et al. with AlO(OH)  $\alpha$  H<sub>2</sub>O precipitate by reaction of Al<sup>3+</sup> nitrate with NH<sub>4</sub>OH [14]. A pure  $\theta$ -Al<sub>2</sub>O<sub>3</sub> appears as early as at 1173 K, with a complete conversion to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, *d* = 45 to 55 nm, at 1453 K. No  $\theta$ -Al<sub>2</sub>O<sub>3</sub> lies at *d* > 25 nm. It can be taken as the *R<sub>c</sub>* value for all practical purposes.



**Fig. 8** Shift in X-ray diffraction peak in (113) reflection in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles with processing temperature at a) 1475 K, b) 1525 K, c) 1700 K, d) 1900 K and e) 1900 K for 2 h, except in d) for 10 min.



Fig. 9 a) A close-up of X-ray diffraction showing the additional peaks present for metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in weak intensity (marked by the asterisks) in the sample annealed at 1700 K for 2 h. b) The peaks in the usual  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are indexed with (hkl).

Although the impurities, dopants, or porosity modify the grain growth and phase transformation, their role in  $R_c$  has not been addressed so far.

Thermodynamically, formation of a solid particle in volume V enclosed in surface area A involves a change in the total Gibbs free energy,

$$\Delta G = A \sigma - \Delta G_{\rm v} V, \tag{2}$$

with  $\Delta G_{\nu}$  (>0) the change in the volume Gibbs free energy per unit volume on its formation from an amorphous state [32]. Assuming a spherical shape of particle of radius r, it can be rewritten as

$$\Delta G = 4\pi r^2 \sigma - \frac{4}{3}\pi r^3 \Delta G_{\nu}.$$
(3)

On dividing by the mass,  $m = \frac{4}{3} \pi r^3 \rho$  (with  $\rho$  the density), it turns into a simple working relation,

$$\Delta G_m^k = \frac{3\sigma}{r\rho} + C_m^k,\tag{4}$$

with  $C_m^k = -\Delta G_v^k \rho^{-1}$  a constant for a polymorph *k*.

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Fig. 10 Gibbs free energy change  $\Delta G_m^k$  in formation of a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, b)  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, and c)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles in a spherical shape. The figure in the inset portrays their  $C_m^k$  energy level diagram at zero surface area.

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Equation (4) represents a monotonically decreasing function of release of the excess structural energy  $\Delta G_m^k$  with grain growth *r*. The  $\Delta G_m^k$  vs. *r* curve in a polymorph *k* differs from the one in the thermodynamic standard state ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub>) primarily in  $C_m^k$ . Extrapolation of the curve to  $r \rightarrow \infty$  gives the value of  $C_m^k$ by the  $\Delta G_m^k$  bulk value. The simulations made with  $\rho = 3.67, 3.58$ , or 3.98 g/cm<sup>3</sup> and  $\sigma = 0.79, 1.58$ , or 2.08 J/m<sup>2</sup> in  $\gamma$ -,  $\theta$ -, or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are portrayed in Fig. 10. An intermediate  $\sigma$ -value of twice that in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> is taken in  $\theta$ -Al<sub>2</sub>O<sub>3</sub> for lack of its known value. A relative  $C_m^k$  value, i.e. 178.4 J/g in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> or 17.1 J/g in  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, used with respect to the  $C_m^{\alpha}$  value (assumed to be zero as usual) in bulk  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> reproduces the experimental  $R_c = 10$  or 25 nm values at which they execute the phase transformation to  $\theta$ -Al<sub>2</sub>O<sub>3</sub> or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The 178.4 J/g value derived for  $C_m^{\gamma}$  compares with the  $\Delta H = 132 \pm 20$  J/g enthalpy proposed in hypothetical coarse-grained  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> relative to bulk  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> using molecular dynamics (MD) simulations [11].

The intersections in curves (a)  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and (b)  $\theta$ -Al<sub>2</sub>O<sub>3</sub> with curve (c)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at points A and B in Fig. 10 determine the critical  $S_m^{\gamma} = 129.1$  and  $S_m^{\theta} = 105.9$  J/g surface energies (after the corrections for the  $C_m^k$  values) below which the particles exist in the involved structures.  $A_m^{\gamma} = 163.5$  and  $A_m^{\theta} = 67.0 \text{ m}^2/\text{g}$  are obtained by their abscissas. This is in agreement with the MD simulations that  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> becomes energetically stable as  $A_m^k$  exceeds  $125 \text{ m}^2/\text{g}$  [11]. As shown by the energy level diagram in the inset to Fig. 10, both of them are surface-stabilized high-energy polymorphs with respect to  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, involving the maximum energy, nucleates and grows first in early sizes to point A. In a non-disrupted growth, the resulting particles convert and grow in  $\theta$ -Al<sub>2</sub>O<sub>3</sub> as an intermediate phase at moderate energy between A and B.  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> appears after point B at  $A_m^k < 67 \text{ m}^2/\text{g}$  (d > 25 nm). It involves  $\gamma$ -and  $\theta$ -Al<sub>2</sub>O<sub>3</sub> phase selection sequence as per  $S_m^k$  energy. Differences in  $S_m^k$  allow the formation and existence of a particular phase at a given temperature.

## 3.4 Vacancy-stabilized α-Al<sub>2</sub>O<sub>3</sub> nanoparticles and twin structure

The  $Al^{3+}$  vacancies (holes) and oxygen-deficient  $AlO_{6-\varepsilon}$  sites determine a metastable  $\alpha$ - $Al_2O_3$  structure. Let us consider an ideal close packing of the atoms in an ideal  $\alpha$ - $Al_2O_3$  structure and then point out small



**Fig. 11** Distribution of Al<sup>3+</sup> cations and holes in a)  $O^{2-}$  layer and b) simple hexagonal lattice in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.  $A_1$ ,  $A_2$ , and  $A_3$  are the basal hexagonal cell vectors. The lattice vectors  $a_1$ ,  $a_2$ , and  $a_3$  describe a rhombo-hedral subcell (after Kronberg [19]).



**Fig. 12** A local model distribution of  $Al^{3+}$  cations and holes in  $AlO_6$  and  $AhO_6$  sites in a plane (*hkl*) in three feasible configurations: a) all  $AlO_6$  sites, b) two  $AlO_6$  and two  $AhO_6$  sites, and c) three  $AlO_6$ and one  $AhO_6$  sites. A modified plane (a) in  $d_{hkl}$ spacing appears in (b) while it splits into two modified planes in a twin structure in (c).

deviations that arise in these defects. It consists of  $R\overline{3}c$  hexagonal unit cell with  $Z = 18 \text{ Al}_2\text{O}_3$  molecules per hexagonal lattice. Distribution of Al<sup>3+</sup> and holes in two O<sup>2-</sup> layers is given in Fig. 11a. The O<sup>2-</sup> forms a near-close-packed hexagonal sublattice and Al<sup>3+</sup> occupies two-thirds of the AlO<sub>6</sub> sites. The unit cell (Fig. 11b) has four consecutive O<sup>2-</sup> layers in average 20 Al<sup>3+</sup> cations and 11 holes.  $A_1$ ,  $A_2$ , and  $A_3$  are the unit lattice vectors in the basal plane.



**Fig. 13** Curing oxygen-deficient structural units from (a)  $AIO_{6-\delta}$ ,  $\delta = 2$ , to (b)  $AIO_6$  by a reaction with (c)  $O^{2-}$  in the mobile  $AhO_6$  hole in a metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. As given in (d)  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, an enhanced dimension appears of  $AIO_6$  if it exists with  $AIO_{6-\delta}$ ,  $\delta \le 0$ , in a high-energy configuration.

An Al<sup>3+</sup> hole (Ah), a region of localized negative charge, is bounded by outer electrons in O<sup>2-</sup> in AhO<sub>6</sub>. The cations and holes are arranged in a manner to give a maximum separation of like charges and a minimum separation of unlike charges as per the Al<sup>3+</sup> and O<sup>2-</sup> bonding, so that the total charge is neutralized. The AhO<sub>6</sub> group thus has a manifested AlO<sub>6</sub> dimension. As shown in Fig. 12, a substitution of AhO<sub>6</sub> in part of the AlO<sub>6</sub> sites raises the separation between the layers from  $d_{hkl}$  to  $d_{hkl'}$ . Two different  $d_{hkd}$  and  $d_{hkl'}$  sets of planes may result at a small  $f^h < 0.36$  fraction of holes, insufficient to fill all of their positions ( $f^h = 11/31 \cong$ 0.36) in the four layers. In this case, at least one layer gets its modified position. A single set of  $d_{hkl}$  or  $d_{hkl'}$ planes exists at  $f^h = 0$  or 0.36. No stable structure exists with holes at  $f^h > 0.36$ . An AlO<sub>6-8</sub> defect causes moderate  $d_{hkl'}$  as it has a smaller size than AlO<sub>6</sub>, e.g., Al<sup>3+</sup> has 0.0675 nm ionic size in AlO<sub>6</sub> while 0.0530 nm in AlO<sub>4</sub> [33].

This model structure describes the X-ray diffraction in metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Table 2), with the same  $R\overline{3}c$  hexagonal structure as in bulk  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. It has larger a = 0.4765 nm and c = 1.3060 nm over the equilibrium a = 0.4742 nm and c = 1.2930 nm values after 2 h of annealing at 1700 K. A non-porous bulk  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> has a = 0.4758 nm and c = 1.2991 nm [25]. The excess volume is relieved by local reordering of atoms in the equilibrium configuration by a structural relaxation [18, 34]. The peaks in metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> in (003), (005), (006), (110), and (112) reflections have relatively larger  $d_{hkl}$  by 0.005 to 0.015 nm over the average values calculated from the average a and c values. These are the hole-sensitive reflections. The (103), (004), and (206) peaks have lower  $d_{hkl}$  values by up to 0.019 nm over the calculated ones. A large atomic relaxation, as much as 0.1 nm, is shown in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> boundary planes through atomistic simulation of the grain boundary structure [20]. It was realized quite early [19, 35] that the Al<sup>3+</sup> displaces towards the vacant sites. The cation sheets are thus puckered or staggered rather than flat. It distorts AlO<sub>6</sub> in different Al–O bonds (Fig. 13).

In Fig. 14, electron diffractograms (a) and (b) in a mesoporous  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> of TEM (c) have a number of twins as marked by the asterisks. They lie at off positions of the regular diffraction points in the regular



(b)



arrays. The results are in accord with the basal slip and twinning observed in HREM images in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [18, 20]. Each of the two boundaries in a basal twin has a different two-dimensional structure. This arises in "splitting of the basal plane" in two  $d_{hkl}$  sets in AhO<sub>6</sub> and AlO<sub>6</sub> size mismatch. Our model gains further support by the fact that the grain boundary or facet planes in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are found to be dense in O<sup>2–</sup> anions [36], i.e., they have significant AhO<sub>6</sub> groups. A problem in studies of twins in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> arises from the fact that a unidirectional shear involving successive displacements of pairs of O<sup>2–</sup> planes does not give a twin [37]. Chen and Howitt [37] proposed successive motion of partial dislocations, while Bilde-Sorensen et al. [38] included cross-slip of the partials to model twin formation in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. Kaplan et al. studied HREM images with energy and grain boundary structure calculations with an ionic model [18]. The twin boundary assumes one of two different configurations, which arise in anisotropic grain growth during twin formation.

The Al<sup>3+</sup> holes and O<sup>2-</sup> ions surrounding a hole in an AhO<sub>6</sub> site appear to be stable at 1475 K. They become effectively mobile at a temperature as high as 1900 K and thus locally react with nearby oxygen-deficient AlO<sub>6- $\sigma$ </sub> groups to cure in regular AlO<sub>6</sub> groups. This is shown in Fig. 13 with  $\delta$  = 2 in AlO<sub>4</sub> group. As in  $\theta$ -Al<sub>2</sub>O<sub>3</sub> [13], the four O atoms in AlO<sub>4</sub> are in three different Al–O bond lengths, 0.1710, 0.1745, and 0.1811 nm. They assume enhanced 0.1969 and 0.1857 nm values [13] in cured AlO<sub>6</sub>. This is well reflected in 1.1 % increase in V in the lattice (Fig. 8e) relative to that in the sample processed at 1700 K (Fig. 8c).

## 3.5 IR spectrum in vacancy-controlled $\alpha$ -Al<sub>2</sub>O<sub>3</sub> structure

IR spectroscopy is a very sensitive analytical tool for analyzing local structure in molecular species and their reordering in a specific structure [39–43]. This is applied here by analyzing whether our metastable



 $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase (obtained at 1475 K) has really a new local structure of AlO<sub>6</sub> groups, or defects of Al<sup>3+</sup> vacancies (in AhO<sub>6</sub> sites) and AlO<sub>6- $\delta$ </sub> architects, or just an intermediate structure in the two phases  $\alpha$ - and  $\theta$ -Al<sub>2</sub>O<sub>3</sub>. To resolve it, we studied the spectra in (a)  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, (b) metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, (c)  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and (d) a 1:1 mixture of (a) and (c). The results compared in Fig. 15 reveal the spectrum in two primary band groups of (i) 300–525 cm<sup>-1</sup> and (ii) 400–1000 cm<sup>-1</sup> as marked by the letters A, B, and C. The shape, size, and internal structure of bands differ markedly in the four samples. For example, band group (i), which extends to 400 cm<sup>-1</sup> in (a), marked by point B, shifts to 475 cm<sup>-1</sup> in (b) and to 525 cm<sup>-1</sup> in (c) or (d). The intensity profile in band group (ii) varies in a near Vshape in (a) and (b), while no such distinct structure persists

**Fig. 15** IR spectra in nanocrystals in (a)  $\theta$ -Al<sub>2</sub>O<sub>3</sub>, b) metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, (c) usual  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, and d) 1:1 mixture in a) and c). The three polymorphs have been annealed for 2 h at 1275 K, 1475 K, and 1525 K, respectively.

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bands (cm <sup>-1</sup> )			assignment	
$\theta$ -Al <sub>2</sub> O <sub>3</sub>	metastable $\alpha$ -Al <sub>2</sub> O <sub>3</sub>	$\alpha$ -Al <sub>2</sub> O <sub>3</sub>	-	
330 (vw)	335 (vw) 366 (w)		$V_2$ (AlO <sub>4</sub> ), deformation	
460 (ww)	448 (ms)	383 (vw)	$v_2$ (AlO <sub>6-<math>\delta</math></sub> ), deformation $v_2$ (AlO <sub>6-<math>\delta</math></sub> ), deformation	
400 (VW)	535 (s)	490 (s) 490 (vw)	$v_2$ (AIO <sub>6</sub> ), deformation $v_4$ (AhO <sub>6-<math>\delta</math></sub> ), deformation	
550 (vs) 610 (s)	580 (vs) 640 (s)	585 (vs) 640 (s) $\int$	$v_4$ (AlO <sub>6</sub> ), deformation	
704 (ms)	712 (ms)	710 (ms)	$v_1$ (AlO <sub>4</sub> )/(AlO <sub>6</sub> ), stretching	
772(8) 820 (vs)	820 (s)	805 (ms)	$v_3$ (AlO <sub>6</sub> ), stretching	
875 (s)	820 (s)		$v_3$ (AlO <sub>4</sub> ), stretching	

**Table 4** Infrared characteristic bands in nanoparticles in the metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> and usual  $\theta$ -Al<sub>2</sub>O<sub>3</sub> and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> polymorphs.

Relative band intensities are given in parentheses: vs, very strong; s, strong; ms, medium strong; w, weak; and vw, very weak.

in other samples. Furthermore, in comparison to (a), a new band (bandwidth  $\Delta v_{1/2} = 30 \text{ cm}^{-1}$ ) has developed at 448 cm<sup>-1</sup> together with an improved energy as well as intensity in the band at 580 cm<sup>-1</sup> (550 cm<sup>-1</sup> in (a)) in (b). A rather broad band,  $\Delta v_{1/2} = 50 \text{ cm}^{-1}$ , at 450 cm<sup>-1</sup> appears with two satellite components at 383 and 490 cm<sup>-1</sup> in (c).

The metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> is thus characterized by an unambiguously different IR spectrum than in  $\theta$ -Al<sub>2</sub>O<sub>3</sub> or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. It does not represent their mixed phase. A mixed  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase, if it exists at all with significant  $\theta$ -Al<sub>2</sub>O<sub>3</sub> (under 50% as per  $I_p$  in the X-ray diffraction peaks in Fig. 7), results in an altogether different and complex spectrum, as shown in Fig. 15d. Assignments of all observed bands in terms of possible modes of vibration in AlO<sub>4</sub> and/or AlO<sub>6</sub> groups are given in Table 4. As can be derived through group theory [39], there are a total of four vibration groups  $v_i$ ,  $i = 0 \rightarrow 4$ , in AlO<sub>4</sub> whereas there are six ( $i = 0 \rightarrow 6$ ) in AlO<sub>6</sub>. Their distributions and symmetry species in T<sub>d</sub> (AlO<sub>4</sub>) and O<sub>h</sub> (AlO<sub>6</sub>) point groups are given in Tables 5 and 6. The occurrence of most of them in the IR spectra in Table 4 infers lowered site symmetry C<sub>1</sub> in AlO<sub>4</sub> and D<sub>2d</sub> or C<sub>1</sub> in AlO<sub>6</sub> in the presumed sublattice distortion. Otherwise, only the v<sub>3</sub> and v<sub>4</sub> bands occur in IR in both AlO<sub>4</sub> and AlO<sub>6</sub>. This is obeyed in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with four bands at 357, 536, 744, and 807 cm<sup>-1</sup> [41].

The doublet band at average 350 cm<sup>-1</sup>, intrinsic to v<sub>2</sub> and v<sub>4</sub> AlO<sub>4</sub> deformation vibrations [39], in spectra (a) and (b) demonstrates AlO<sub>4</sub> groups to be present in metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> as well. The ratio ( $F_{tt0}$ ) of AlO<sub>4</sub>/AlO<sub>6</sub> is 1:2 in  $\theta$ -Al<sub>2</sub>O<sub>3</sub> [13]. While heating at 1475 K, part of the AlO<sub>4</sub> in it converts to AlO<sub>6</sub> with the phase transformation to the metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. This reflects a drastic increase in intensity in

Table 5	Distribution of four fundamental molecular vibration groups in $AlO_4$ structural unit in $Al_2O_3$ .

mode	symmetry sp	ecies				
	point group (T <sub>d</sub> )		site symmetry (C <sub>1</sub> )		factor group (D <sub>2d</sub> )	
$v_1$	$A_{1}(R)$				$A_1(\mathbf{R})$	
$V_2$	E (R)		$A_1(\mathbf{R}, \mathbf{IR})$		$B_1(\mathbf{R})$	
$V_3$	$F_2(R, IR)$	$\sim$			$B_2(IR, R)$	
$V_4$	$F_2(R, IR)$	/			E(IR, R)	

R, Raman-active; and IR, infrared-active vibrations. Vibration  $v_2$  is doubly degenerate while  $v_3$  and  $v_4$  are triply degenerate in the total of nine vibrations.

mode species  $C_1$  $T_d$ point group  $(O_h)$  $A_{1g}(R)$  $A_1(R)$  $v_1$  $E_{g}(R)$ E (R)  $v_2$  $F_{1u}(IR)$  $A_1(R, IR)$  $F_2(R, IR)$  $V_{3}, V_{4}$  $F_{2g}(R)$  $F_2(R, IR)$  $V_5$  $F_{2u}$  (IA)  $F_1$  (IR)  $v_6$ 

**Table 6** Distribution of six fundamental molecular vibration groups in AlO<sub>6</sub> structural unit in  $O_h$ ,  $T_d$  and  $C_1$  point groups.

R, Raman-active; IR, infrared-active; and IA, inactive vibrations. Vibration  $v_2$  is doubly degenerate while  $v_3$  to  $v_6$  are triply degenerate in the total of 15 vibrations.

the characteristic band  $v_2$  at 448 cm<sup>-1</sup> (or  $v_4$  at 580 cm<sup>-1</sup>) at the expense of that in the  $v_3$  (AlO<sub>4</sub>) band at 875 cm<sup>-1</sup>. A fractional value of AlO<sub>4</sub> groups of

$$F_{t}^{k} = \kappa \frac{I_{t}}{I_{t} + I_{0}} \sim 18\%$$
(5)

is obtained from relative intensities  $I_t$  and  $I_0$  in the 366 and 448 cm<sup>-1</sup> bands in two sites in metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The constant  $\kappa = 0.475$ , derived with  $F_t^k = \frac{1}{3}$  with  $I_t$  and  $I_0$  in the  $\theta$ -Al<sub>2</sub>O<sub>3</sub> bands, is used. Another band at 535 cm<sup>-1</sup>, which lies as a shoulder of  $v_4$  (AlO<sub>6</sub>) band at 580 cm<sup>-1</sup> in metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, is ascribed to the  $v_4$  band in Al<sup>3+</sup> holes in AhO<sub>6</sub> sites. It disappears on raising the temperature to 1525 K (Fig. 15c) as the holes become mobile at this temperature, presumably recombining to AlO<sub>4</sub> architect defects,  $F_t^k \sim 18\%$ , to cure into regular AlO<sub>6</sub> groups. This is accompanied with a concomitant decrease in  $I_t$  in the 800–900 cm<sup>-1</sup> region (marked by the downward arrow in Fig. 15) with an increase in  $I_0$  in the band at 585 cm<sup>-1</sup>. Moreover, two new bands developed with an extremely weak intensity at 383 and 490 cm<sup>-1</sup> (in  $v_2$  and  $v_4$  vibrations in Table 4) in a modified force field in trace of AhO<sub>6- $\delta$ </sub> sites in coupling with neighboring Al<sup>3+</sup> cations. Other AhO<sub>6</sub> vibrations do not appear in distinct bands in overlapping with AlO<sub>6</sub> bands.

# 4 Conclusions

Thermodynamically stable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles in support with high-energy surface and Al<sup>3+</sup> vacancies form at a controlled porosity, 10–25%, in a mesoporous structure. The structure is analyzed and modeled with X-ray diffraction, microstructure, and IR spectrum. The synthesis carried out with a monolithic AlO(OH) *x* H<sub>2</sub>O precursor powder (mesoporous) precludes the possibility of other structural inclusions. Unusually, the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> nanoparticles arranged through immobile pores (5–15 nm diameter) behave as highly stable in a confined size of 30–50 nm diameter. Otherwise, they readily grow as big as several hundred nanometers in bulk sample [11, 12] at temperatures as high as 1900 K. The configurational entropy predominates the enthalpy to inhibit their confined growth in a thermodynamically stable structure.

The specimen obtained at moderate temperature, ~1475 K, has copious structural defects of oxygendeficient AlO<sub>6- $\delta$ </sub>,  $\delta \le 2$ , groups and Al<sup>3+</sup> vacancies (negatively charged holes) in octahedral AhO<sub>6</sub> sites in a metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> structure. The like or unlike charges arrange themselves at a maximum or minimum separation by neutralizing their total value. A hole thus reassumes a manifested AlO<sub>6</sub> dimension. It is modeled that an uneven distribution of holes in a specific (*hkl*) plane triggers it in a modified structure. This accords with the X-ray diffraction observed with additional peaks relative to those in bulk  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. A similar twin structure has been observed in selected area electron diffraction and high-resolution electron microscopic images in bulk  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> [18, 20]. The average concentration in it is not sufficient to show up in X-ray diffraction. The metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> phase has 2.0% excess volume over the equilibrium value in nanoparticles after annealing (reorders holes and occupied sites by recovering AlO<sub>6- $\delta$ </sub> defects) at temperatures as high as 1700 K. It is characterized with a different vibrational structure than in  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>.

A mobile  $Al^{3+}$  hole in a site neighboring an  $AlO_{6-\delta}$  defect promotes a plane slipping or a twin structure formation. The dislocation moves into a region of the particle along the  $AlO_{6-\delta}$  defects and not along the reverse direction. It is found that the  $O^{2-}$  in the hole becomes mobile in metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at 1525 K or above, and thus reacts with the defects to cure into a regular AlO<sub>6</sub> polyhedron. A characteristic Ah–O deformation vibration  $v_4$  observed at 535 cm<sup>-1</sup> (580 cm<sup>-1</sup> in AlO<sub>6</sub>) in the IR spectrum in metastable  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> characterizes the holes to be exclusively present in AhO<sub>6</sub> sites. Its relative intensity with respect to that in  $\theta$ -Al<sub>2</sub>O<sub>3</sub> ( $F_{tt0} \sim 33\%$ ) determines a fractional  $F_{tt0} \sim 18\%$  value of  $Al^{3+}$  in AlO<sub>6- $\delta$ </sub>,  $\delta \sim 2$ . Two weak bands developed at the expense of this band in  $v_2$  and  $v_4$  vibrations at 383 and 490 cm<sup>-1</sup> in trace of AhO<sub>6- $\delta$ </sub> in a modified force field in cured  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> at 1525 K.

The results demonstrate the possibilities of varying the microstructure and related properties of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> following controlled grain growth and self-induced pinnings of the local structures through mesopores. The AlO<sub>6- $\delta$ </sub> defects and Al<sup>3+</sup> holes provide sites for initiation and also arrest of self-confined cracks, designing a strengthened structure. The pores act as local pinning barriers to a non-disrupted crack propagation. Otherwise, it grows to be non-disrupted through several grains.

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