Homogeneous nucleation of corundum nanocrystallites by rapid heating of aluminum formate hydroxide-based precursor powder

Michiyuki Yoshida1*, Yuta Kato2, Yasunori Oumi3, Osamu Sakurada1, Makoto Tanaka2, Masashi Wada2 & Satoshi Kitaoka2

The high density nucleation of $\alpha$-Al$_2$O$_3$ nanocrystallites was observed by rapid heating of the aluminum formate hydroxide-based precursor powder at 1200 °C for 50 s. The nucleation of $\alpha$-Al$_2$O$_3$ nanocrystallites with less 10 nm in size from high purity aluminum oxide matrix has not been observed to our knowledge. Based on the results of XRD and TEM, $\alpha$-Al$_2$O$_3$ nanocrystallites nucleated from the amorphous phase which formed after thermal decomposition of the precursor powder. Subsequently, $\alpha$-Al$_2$O$_3$ with hollow rod-like morphology formed through coalescence and growth of nanocrystallites after heating at 1200 °C for 1 min. The results obtained in this paper indicates a possible beneficial effect of the rapid heating and cooling of the aluminum formate hydroxide-based precursor powder on the precipitation of $\alpha$-Al$_2$O$_3$ nanocrystallites.

Aluminum oxide (Al$_2$O$_3$) has various structural polymorphs. The most stable phase of $\alpha$-Al$_2$O$_3$ (corundum, sapphire) is an extremely important material due to its great hardness, high thermal stability and chemical inertness. These excellent properties and stable mass production techniques have led it to be widely applied in the refractory industry. Moreover, $\alpha$-Al$_2$O$_3$, with purity of 99.99% has been applied to advanced ceramics for many functional applications such as the highly fluorescent oxide ceramics and the fillers to improve the durability of resin. High-purity $\alpha$-Al$_2$O$_3$ is synthesized by thermal decomposition of ammonium alum2,3 and hydrolysis of aluminum alkoxide4,5. In these processes, so-called transition phases (denoted as $\gamma$, $\eta$, $\delta$, $\upsilon$) form prior to $\alpha$-Al$_2$O$_3$6–10. The crystal structures of these phases can be classified by the oxygen sublattice and the interstitial sites for aluminum ion. Metastable phases are based on face-centered cubic packing of Oxygen (fcc) with aluminum ions in tetrahedral and octahedral interstitial sites. $\alpha$-Al$_2$O$_3$ has a rhombohedral structure where the oxygen ions form a compact hexagonal sublattice with aluminum ions occupying 2/3 of the octahedral interstitial sites.

It is well known that $\alpha$-Al$_2$O$_3$ nucleation within transition phases is sporadic rather than uniform11,12. Therefore, the calcination above the temperature of 1200 °C for several hours is necessary to achieve a complete transformation to $\alpha$-Al$_2$O$_3$. Higher calcination temperature promotes mass transport, and causes difficulties to obtain fine particles and morphological control. Many efforts have been made to achieve uniform nucleation of $\alpha$-Al$_2$O$_3$. The seeding of the precursor is a common route to increase nucleation density. Rajendran13, in a study of production of ultrafine $\alpha$-Al$_2$O$_3$ powder from aluminum nitrate, found that with $\alpha$-Al$_2$O$_3$ seed in the dry gel of aluminum hydroxide, the temperature of the $\gamma$-Al$_2$O$_3$ to $\alpha$-Al$_2$O$_3$ phase transformation was lowered to 950 °C. Due to the relatively low $\alpha$-Al$_2$O$_3$ formation temperature, the particle size of synthesized $\alpha$-Al$_2$O$_3$ powder was 60 nm. But the observed nucleation behavior of $\alpha$-Al$_2$O$_3$ was not uniform and still sparse. Sanxu14 reported that $\alpha$-Al$_2$O$_3$ nanoparticles were uniformly nucleated in $\alpha$-Fe$_3$O$_4$ matrix by heating the $\alpha$-Al$_2$O$_3$ precursor powder with Fe$_3$+ /Al$_{2+}$ molar ration of 5 at the temperature of 770 °C. By removing $\alpha$-Fe$_3$O$_4$ matrix through selective corrosion, disperse equiaxed $\alpha$-Al$_2$O$_3$ nanoparticles with an average sizes below 10 nm and narrow size distributions were obtained. But this separation process is complicated and the experimental operations are difficult. To our knowledge, uniform nucleation of $\alpha$-Al$_2$O$_3$ nanocrystallites in aluminum-oxide matrix has not been reported.

Recently, the metal organic precursor of aluminum formate has been studied as a simple and innovative approach to synthesize $\alpha$-Al$_2$O$_3$ powder15,16. The advantage of this organometallic precursor is that the complete...
transformation to $\alpha$-Al$_2$O$_3$ can be achieved in relatively lower temperature than reported in aluminum hydroxide based precursor. In this article, we present high density nucleation of $\alpha$-Al$_2$O$_3$ nanocrystallites with less 10 nm in size from high purity aluminum oxide matrix by rapid heating of the aluminum formate hydroxide-based precursor powder. $\alpha$-Al$_2$O$_3$ with hollow rod-like morphology finally formed through coalescence and growth of nanocrystallites after heating at 1200 °C for 1 min.

**Methods**

Al(NO$_3$)$_3$ 9H$_2$O (GR Nacalai tesque), ammonia solution (GR Nacalai tesque), and HCOOH (GR Nacalai tesque) were used as raw materials to prepare $\alpha$-Al$_2$O$_3$. To prepare the precipitate of Al(OH)$_3$, the pH of 0.5 M aluminum nitrate aqueous solution was adjusted to 6 by adding 1.5 M ammonia solution. The gel-like precipitate was separated from the supernatant solution by centrifugation and washed by deionized water. Subsequently, HCOOH was added to the precipitate. The molar ratio of Al to HCOOH was 1 to 3. They were continuously stirred for 1 h and eventually turned into a transparent solution. The prepared transparent solution was dried in the oven at 150 °C for 24 h to prepare the precursor powder.

Pt crucible, which is 1 cm in diameter and 2 cm in height, was filled with 0.6 g of the precursor powder. The perpendicularly arranged tube furnace was heated to the temperature of 1200 °C in advance and then the Pt crucible hanged with Pt wire put into the furnace in 1 s. After the isothermal annealing for 10–100 s, the Pt crucible was removed from the furnace and quenched on the water cooled Cu plate. To prevent the reaction between Pt crucible and Cu plate, Al$_2$O$_2$ powder was placed on the Cu plate.

Phase identifications were performed by Rigaku MiniFlex600 X-ray powder diffraction (XRD) using CuK$\alpha$ radiation in the range of 2$\theta$ = 10–70° with a scanning speed of 2 °/min. The calcined powders were mixed with ethanol to make a suspension and subsequently a few droplets of it were used for microstructure evaluation by JEOL EM-2100 transmission electron microscopy (TEM). The change in the local structure of Al atoms during the transformation to $\alpha$-Al$_2$O$_3$ was evaluated by $^{27}$Al MAS NMR technique. $^{27}$Al MAS NMR spectra were recorded by Bruker AVANCE III 500 spectrometer at 130.318 MHz with 15 kHz spinning speed, 4.0 μs pulses and 1 s relaxation time for 1,000 scans. 1.0 M AlCl$_3$ aqueous solution was used as a chemical shift reference (0.1 ppm).

**Results**

Figure 1(a) shows XRD spectra of the precursor powder. Except for the peak at 2$\theta$ = 36° and some minor peaks in 2$\theta$ < 44°, the main crystal phase of the precursor powder was identified as aluminum formate hydroxide (Al(HCOO)$_2$(OH)). Figure 1(b) shows the SEM micrograph of the precursor powder. The grains with rod-like morphology aggregated to make a flower-like structure.

Figure 2(a) shows a series of XRD spectra for the samples during transformation to $\alpha$-Al$_2$O$_3$ at 1200 °C. For comparison, the peaks of $\alpha$-Al$_2$O$_3$ (JCPDF No. 01-080-0786) are also shown in Fig. 2(a). The peak intensities of $\alpha$-Al$_2$O$_3$ (2$\theta$ = 43.3°), $\gamma$-Al$_2$O$_3$ (2$\theta$ = 67.6°), and Al(HCOO)$_2$(OH) (2$\theta$ = 17.8°) for the samples heated for different
soaking time are shown in Fig. 2(b). The samples maintained a powder state (not sintered) after an isothermal annealing for 10–100 s. When the sample was heated for 10 s, the peaks corresponding to Al(HCOO)_2(OH) were detected. With increasing the soaking time to 30 s, no peaks were detected, indicating that aluminum formate was completely converted to amorphous alumina. With further increasing the soaking time to 50 s, the peaks corresponding to \( \alpha \)-Al_2O_3 appeared, and the quite weak peaks corresponding to \( \gamma \)-Al_2O_3 were also detected. Subsequently, the peaks of \( \gamma \)-Al_2O_3 disappeared, and single phase of \( \alpha \)-Al_2O_3 was obtained over 70 s duration. The crystallite size of \( \alpha \)-Al_2O_3 estimated by Scherrer equation from (113) reflection varies from 38.7 to 42.7 to 40.9 nm on increasing the soaking time from 50 s to 70 s to 100 s (Supplementary data 1). The crystal densities of \( \alpha \)-Al_2O_3 obtained from XRD for 50 s, 70 s and 100 s exhibited 3.99, 3.98 and 3.97 g/cm^3, respectively. The crystal densities in the respective samples were higher than those of the transient phases (\( \gamma \): 3.40 g/cm^3 and \( \theta \): 3.58 g/cm^3) and comparable to the reported value of \( \alpha \)-Al_2O_3 (3.98 g/cm^3)6,8 (Supplementary data 2).

Figure 3 shows \( ^{27} \)Al MAS NMR spectra for the precursor powders calcined at 1200 °C with various soaking time. For comparison, the result for the precursor powder is also shown in Fig. 3. The broad bands of the precursor powder observed at 9.91, −7.06 and −41.82 ppm could be attributed to octahedral aluminum species (Al_{oct}). After calcination for 10 s, the bands at −7.06 and −41.82 ppm decreased drastically and new bands were observed at 38.79 and 74.54 ppm which were attributed to pentavalent (Al_{pva}) and tetrahedral (Al_{tva}) aluminum species, respectively\(^17\). The bands at 9.91 ppm could be derived from the bidentated bond between aluminum and carboxyl group, while the peaks at −7.06 and −41.82 ppm could be associated with hydrogen bonds between water and aluminum formate\(^17\). From the observation of the band attributed to pentavalent aluminum species (Al_{pva}) not present in crystalline phases\(^18\), a part of aluminum formate was converted to amorphous alumina by calcination for only 10 s. With increasing the soaking time to 30 s, the bands at −7.06 and −41.82 ppm completely disappeared. The observed bands at 7.67, 39.29 and 74.39 ppm suggest that three types of the chemical state of aluminum species are in the amorphous alumina. With increasing the soaking time to 50 s, the spectra showed the typical signal of Al_{tva} in \( \alpha \)-Al_2O_3, and the band attributed to Al_{pva} disappeared. The shoulder peak at 8 ppm produced by Al_{tva} in \( \gamma \)-Al_2O_3, and the second peak at 69.38 ppm corresponding to Al_{tva} in \( \gamma \)-Al_2O_3 were also observed in the sample soaked for 50 s\(^15\). This is consistent with the XRD result (Fig. 2(a)). With further increasing the soaking time, the bands attributed to Al_{tva} and Al_{pva} in \( \gamma \)-Al_2O_3 disappeared and finally, a single band attributed to the octahedral aluminum species in \( \alpha \)-Al_2O_3 was detected at 14.07 ppm\(^19\). These results are in consistence with the previous report of \( ^{27} \)Al MAS NMR spectra for aluminum formate calcined at 200–1500 °C\(^12\).

Figure 4 shows TEM micrographs of the samples heated for 30 s, 50 s and 100 s, and then quenched from 1200 °C. The rod-like grains originated from the precursor powder were observed in the sample heated for 30 s.
as shown in Fig. 4(a). The high magnification image for 30 s showed the sparse nucleation of nanocrystallites in the rod-like grain. When the sample was heated for 50 s, the higher density of nucleation of nanocrystallites was observed in the rod-like grains. Moreover, a sea of nanocrystallites were also observed around the rod-like grains (indicated with white arrow in Fig. 4(b)). This might be the artifact during the preparation of TEM sample. These nanocrystallites observed on the collodion film are supposed to drop out of rod-like grains in the ethanol suspension. In the sample heated for 100 s, nanocrystallites were not observed and the hollow tubular structure was observed in the rod-like grains.

Discussion

Figure 5(a) shows the high magnification TEM image around the rod-like grains in Fig. 4(b). The TEM image of the nanocrystallites obtained at 1200 °C for 50 s revealed that the nanocrystallites are disperse and almost equiaxed in shape. The SAED analysis of the nanocrystallites in Fig. 5(a) shows a typical diffraction pattern of $\alpha$-$\text{Al}_2\text{O}_3$. The size distribution histogram of the $\alpha$-$\text{Al}_2\text{O}_3$ nanocrystallites [Fig. 5(b)] was determined by image analysis of the TEM images taken from about 700 particles. It revealed that the $\alpha$-$\text{Al}_2\text{O}_3$ nanocrystallites had a mean size of 5.7 nm and a size distribution from 1.6 to 15.4 nm. The size distribution width of the $\alpha$-$\text{Al}_2\text{O}_3$ nanocrystallites was narrow. The vermicular microstructure reported in literature was sometimes observed in our samples, but the size of the structure was not more than 10 nm, which was about one tenth of that reported in the literature. These results suggested that the critical particle size for $\alpha$-$\text{Al}_2\text{O}_3$ was ~10 nm in this study.

It was previously reported that $\gamma$ to $\alpha$ phase transformation occurs by nucleation and growth processes in the $\gamma$-$\text{Al}_2\text{O}_3$ matrix. The critical particle size for the $\gamma$ to $\alpha$ transformation depends on the surface free energy of the alumina phases. Increases in the Gibbs free energy of the alumina particles resulting from their small radii of curvature can be expressed as:

$$G = G^0 + 2\gamma V^0/\rho$$

(1)

where $G$ is the Gibbs free energy of an alumina particle with radii of curvature $\rho$, $\gamma$ is surface energy, $G^0$ is the standard Gibbs free energy, and $V^0$ is the molecular volume. According to the literature, the surface energy for $\alpha$-$\text{Al}_2\text{O}_3$ (1.98 kJ/mol) was significantly higher than those of $\gamma$-$\text{Al}_2\text{O}_3$ (0.79 kJ/mol). Therefore, preferential exposure of the surfaces with lowest energy, $\gamma$-$\text{Al}_2\text{O}_3$ should become the energetically stable polymorph in the particle size below 11 nm at 1200 °C as shown in Fig. 6. This value corresponds approximately to the reported critical diameter of $\alpha$-$\text{Al}_2\text{O}_3$. According to the TEM image (Fig. 5(a)), the critical diameter of $\alpha$-$\text{Al}_2\text{O}_3$ was much smaller than that reported in the literature.

The crystal structure of $\gamma$-$\text{Al}_2\text{O}_3$ is based on face-centered cubic packing of Oxygen (fcc), while the packing of Oxygen for $\alpha$-$\text{Al}_2\text{O}_3$ is based on hexagonal close packing structure (hcp). It has been proposed that the activation energy for the $\gamma$ to $\alpha$ transformation is related primarily to the rearrangement of oxygen sublattice. This difference in the crystal structure between $\gamma$-$\text{Al}_2\text{O}_3$ and $\alpha$-$\text{Al}_2\text{O}_3$ results in a disadvantage of $\gamma$-$\text{Al}_2\text{O}_3$ as the intermediate phase transforming to $\alpha$-$\text{Al}_2\text{O}_3$. As clearly seen in the XRD result of Fig. 2(a) and the TEM micrograph of Fig. 4(a), $\alpha$-$\text{Al}_2\text{O}_3$ nanocrystallites nucleated from the amorphous phase. In $^{27}$Al MAS NMR spectrum of the amorphous phase, the strong band and the broad bands attributed to octahedral ($\text{Al}_{\text{VI}}$), pentavalent ($\text{Al}_{\text{V}}$)}
and tetrahedral (Al IV) aluminum species were observed. It is well known that the local structure of aluminum atoms in $\alpha$-$\text{Al}_2\text{O}_3$ is octahedral, while $\gamma$-$\text{Al}_2\text{O}_3$ is composed of both octahedral and tetrahedral coordinated aluminum atoms. The amorphous phase has no long range order, and the local structure of aluminum atoms in the amorphous phase is different from that in the crystalline phases. Nevertheless, the amorphous phase can easily transform to $\alpha$-$\text{Al}_2\text{O}_3$ phase in a quite short calcination time. It has been reported that $\alpha$-$\text{Al}_2\text{O}_3$ nanocrystallites with a size under 10 nm nucleate from $\alpha$-$\text{Fe}_2\text{O}_3$ matrix, which has the same crystal structure with $\alpha$-$\text{Al}_2\text{O}_3$.

These results suggested that the intermediate phase of the amorphous which formed through

Figure 4. TEM micrographs of the samples heated at 1200 °C for 30 s (a), 50 s (b) and 100 s (c). The inset right below in (a) is the high magnification image showing the sparse nucleation. The inset left above in (b) highlights the high density nucleation of $\alpha$-$\text{Al}_2\text{O}_3$ nanocrystallites. The inset left above in (c) is the low magnification image indicating the morphology of the aggregate.
the thermal decomposition of the aluminum formate hydroxide had lower activation barrier to form $\alpha$-Al$_2$O$_3$ phase than that of the transition phases, and resulted in the nucleation of $\alpha$-Al$_2$O$_3$ with the size under 10 nm. On the other hand, the crystallite size of $\alpha$-Al$_2$O$_3$ obtained by Scherrer equation in Fig. 2(a) for 50 s was 38.7 nm which was larger than the estimated critical diameter of 11 nm in the nucleation from the transition phase in Fig. 6. Considering the estimation of crystallite size in XRD, it is not sure whether the amorphous phase has the lower activation barrier to form $\alpha$-Al$_2$O$_3$ than the transition phases. We do not have the valid explanation of this discrepancy between TEM micrograph and XRD in crystallite size. The careful discussion is needed to clarify the critical particle size of $\alpha$-Al$_2$O$_3$ during the rapid heating of this precursor powder.

Figure 7 shows the schematic images of the microstructural evolution during the formation of the rod-like $\alpha$-Al$_2$O$_3$. The agglomerations of the aluminum formate hydroxide particles were thermally decomposed to
form the amorphous phase (Figs 1(b), 4(a)). Subsequently, the highly condensed nucleation of nanocrystallites was observed in the rod-like grains (Fig. 4(b)). Finally, the hollow tubular structure was observed in the grains (Fig. 4(c)). The observed hollow tubular structure suggests that $\alpha$-Al$_2$O$_3$ nanocrystallites preferentially nucleate at the surface of the grains. $\alpha$-Al$_2$O$_3$ powder is usually prepared by heat treatment of aluminum hydroxide such as Boehmite which strongly differ from each other in the morphology of the particles, depending on the conditions of synthesis. In the case of Boehmite, a calcination above 1200 °C for several hours is necessary for the complete transformation to $\alpha$-Al$_2$O$_3$ due to the higher nucleation barrier\textsuperscript{24}. Higher transformation temperature resulted in the activation of the mass transport which resulted in the deterioration of the controlled morphology of the particles. In our precursor powder, single phase of $\alpha$-Al$_2$O$_3$ was successfully obtained in a quite short calcination time (about 1 min). The rod-like morphology of the precursor powder was maintained after a calcination achieving the complete transformation to $\alpha$-Al$_2$O$_3$. The rod-like hollow $\alpha$-Al$_2$O$_3$ is relatively lightweight and supposed to be easy to create three-dimensional network in the resin. Therefore, the rod-like hollow $\alpha$-Al$_2$O$_3$ is expected to be a candidate material for a highly thermal conductive filler in power device.

In our previous report\textsuperscript{16}, the complete transformation to $\alpha$-Al$_2$O$_3$, successfully achieved by the normal furnace heating (5 °C/min) of the precursor powder consisting of aluminum formate hydroxide at 950 °C for 24 h, which is about 200 °C lower than that reported in the typical precursor of aluminum hydroxide. During the transformation to $\alpha$-Al$_2$O$_3$ at 950 °C, nanocrystallites were not observed in the sample by TEM. Although the high density nucleation of $\alpha$-Al$_2$O$_3$ nanocrystallites was observed in the sample heated at 1200 °C for 50 s, the resulting $\alpha$-Al$_2$O$_3$ was not 100% phase pure. The residual amorphous phase and $\gamma$-Al$_2$O$_3$ persists. The results obtained in this paper indicates a possible beneficial effect of the rapid heating and cooling on the precipitation of $\alpha$-Al$_2$O$_3$ nanocrystallites. As well as a raw material for the advanced nanoceramics, $\alpha$-Al$_2$O$_3$ nano-particles are expected to be a candidate material for reducing environmental load such as catalyst support, gas separation membrane module and a filler for transparent resin which facilitates the development of lightweight vehicle. We believe the combination of this precursor powder and the common rapid heating techniques such as IR, laser and gas burner would popularize a quantity synthesis of $\alpha$-Al$_2$O$_3$ nano particles. To obtain 100% phase pure $\alpha$-Al$_2$O$_3$ nano particles, it is necessary to optimize the synthesis conditions such as calcination temperature and heating rate.

Figure 7. The microstructural evolution of the sample during the transformation to $\alpha$-Al$_2$O$_3$: (a) the agglomeration of the rod-like aluminium formate hydroxide particles (Fig. 1(b)), (b) the precursor powder was thermally decomposed to form the amorphous phase (Fig. 4(a)), (c) the highly condensed nucleation of nanocrystallites in the rod-like grains (Fig. 4(b)) and (d) $\alpha$-Al$_2$O$_3$ grains with hollow rod-like structure (Fig. 4(c)).
Conclusions
Homogeneous nucleation of $\alpha$-$\text{Al}_2\text{O}_3$ nanocrystallites with less than 10 nm in size through rapid heating of the aluminum hydroxide-based precursor powder was observed by TEM. $\alpha$-$\text{Al}_2\text{O}_3$ nanocrystallites nucleated from the amorphous phase which formed after thermal decomposition of the precursor powder. $^{27}$Al MAS NMR spectra for the amorphous phase showed the strong band and the broad bands attributed to octahedral ($\text{Al}_I$) and tetrahedral ($\text{Al}_II$) aluminum species. These results suggested that the local structure of aluminum atoms in the intermediate phase of the amorphous was different from that in the crystalline phases. The crystallite size of $\alpha$-$\text{Al}_2\text{O}_3$ observed by TEM in the sample heated for 50 s at 1200 °C was smaller than the estimated critical diameter of 11 nm in the nucleation from the transition phase according to thermodynamics. On the other hand, the crystallite size of $\alpha$-$\text{Al}_2\text{O}_3$ obtained by Scherrer equation exhibited 38.7 nm in the sample heated for 50 s at 1200 °C. There was a discrepancy between TEM micrograph and XRD in crystal size. Single phase of $\alpha$-$\text{Al}_2\text{O}_3$ was successfully obtained in a quite short calcination time (about 1 min). The rod-like morphology of the precursor powder was maintained after a calcination achieving the complete transformation to $\alpha$-$\text{Al}_2\text{O}_3$. The results obtained in this paper indicates a possible beneficial effect of the rapid heating and cooling on the precipitation of $\alpha$-$\text{Al}_2\text{O}_3$ nanocrystallites. The combination of this precursor powder and the common rapid heating techniques would popularize a quantity synthesis of $\alpha$-$\text{Al}_2\text{O}_3$ nano particles.

Received: 17 June 2019; Accepted: 24 September 2019;
Published online: 17 October 2019

References
1. Wefers, K. & Misra, C. Oxides and Hydroxides of Aluminum, Alcoa Technical Paper No. 19, Alcoa Laboratories, Pittsburgh, PA (1987).
2. Dynys, F. W. & Halloran, J. W. Alpha alumina formation in alum-derived gamma alumina. J. Am. Ceram. Soc. 65, 442 (1982).
3. Morinaga, K., Torikai, T., Nakagawa, K. & Fujino, S. Fabrication of fine $\alpha$-alumina powders by thermal decomposition of ammonium aluminum carbonate hydroxide (AACH). Acta mater. 48, 4733 (2000).
4. Yoldas, B. E. Effect of variations in polymerized oxides on sintering and crystalline transformations. J. Am. Ceram. Soc. 65, 387 (1982).
5. Sharma, P. K., Varadan, V. V. & Varadan, V. K. A critical role of pH in the colloidal synthesis and phase transformation of nano size $\alpha$-$\text{Al}_2\text{O}_3$ with high surface area. J. Eur. Ceram. Soc. 23, 659 (2003).
6. Levin, I. & Brandon, D. Metastable alumina polymorphs: crystal structures and transition phases. J. Am. Ceram. Soc. 81, 1995 (1998).
7. Ram, T. Self-confined dimension of thermodynamic stability in Co-nanoparticles in FCC and BCC allotropes with a thin amorphous $\text{Al}_2\text{O}_3$ surface layer. Acta mater. 49, 2297 (2001).
8. Mohanty, P. & Ram, S. Confined growth of $\text{Eu}_2\text{O}_3$ nanocrystals in a new polymorph in amorphous mesoporous $\text{Al}_2\text{O}_3$. Phil. Mag. B 82, 1129 (2002).
9. Rana, S. & Ram, S. Self-controlled growth in highly stable $\alpha$-$\text{Al}_2\text{O}_3$ nanoparticles in mesoporous structure. Phys. Stat. Sol. (a) 201, 427 (2004).
10. Ram, S., Mishra, A. & Fecht, H. J. Radiative emissions in rare-earth ions in $\text{Al}_2\text{O}_3$ and nanocomposite. Encyclopedia of Nanoscience & Nanotechnology 22, 179 (2011).
11. Gao, Y. & Nieh, T. G. Nucleation and concurrent anomalous grain growth of $\gamma$-$\text{Al}_2\text{O}_3$ during $\gamma\rightarrow\alpha$ phase transformation. J. Am. Ceram. Soc. 74, 2270 (1991).
12. Bagwell, R. B. & Messing, G. L. Effect of seeding and water vapor on the nucleation and Growth of $\alpha$-$\text{Al}_2\text{O}_3$ from $\gamma$-$\text{Al}_2\text{O}_3$. J. Am. Ceram. Soc. 82, 825 (1999).
13. Rajendran, S. Production of ultrafine alpha alumina powders and fabrication of fine grained strong ceramics. J. Mater. Sci. 29, 5664 (1994).
14. Santhi, S., Li, L., J., Ji, M., Fuliang, L. & Jiangong, L. Disperse fine equalized alpha alumina nanoparticles with narrow size distribution synthesised by selective corrosion and coagulation separation. Sci. Rep. 5, 11575 (2015).
15. Reyes-López, S. Y., Acuña, R. S., López-Juárez, R. & Rodríguez, J. S. Analysis of the phase transformation of aluminum formate $\text{Al(O}_2\text{CH)}_3$ to $\alpha$-alumina by Raman and infrared spectroscopy. J. Ceram. Process. Res. 14, 627 (2013).
16. Yoshida, M. et al. Powder Technol. Japan 53, 571 (2016).
17. Roque-Ruiz, J. H., Cabrera-Ontiveros, E. A., González-García, G. & Reyes-López, S. Y. Thermal degradation of aluminum formate sol-gel; synthesis of $\alpha$-alumina and characterization by $^1\text{H}$, $^{13}\text{C}$ and $^{27}\text{Al}$ MAS NMR and XRD spectroscopy. Results Phys. 6, 1096 (2016).
18. O’Dell, L. A., Savin, S. L. P., Chadwick, A. V. & Smith, M. E. A. $^{27}$Al MAS NMR study of a sol–gel produced alumina: Identification of the NMR parameters of the $\theta$-$\text{Al}_2\text{O}_3$ transition alumina phase. Solid State Nucl. Mag. 31, 169 (2007).
19. Yakovlev, I. V. et al. Stabilizing effect of the carbon shell on phase transformation of the nanocrystalline alumina particles. Ceramics International 44, 4801 (2018).
20. Adamson, A. W. In Physical Chemistry of Surfaces. 5th edition, John Wiley and Sons (1990).
21. Marmier, A. & Parker, S. C. Ab initio morphology and surface thermodynamics of $\alpha$-$\text{Al}_2\text{O}_3$. Phys. Rev. B 69, 115409 (2004).
22. Méhalle, J. M., Aureouze, A., Perrotta, A. J. & Navrotsky, A. Surface Energies and Thermodynamic Phase Stability in Nanocrystalline Aluminas. Science 277, 788 (1997).
23. Chang, P. L., Yen, F. S., Cheng, K. C. & Wen, H. L. Examinations on the critical and primary crystallite sizes during $\theta$- to $\gamma$-phase transformation of ultrafine alumina powders. Nano Lett. 1, 253 (2001).
24. Iler, R. K. Fibrous colloidal boehmite; Progressive conversion to gamma, theta, and alpha aluminas. J. Am. Ceram. Soc. 44, 618 (1961).

Acknowledgements
This work was supported by the Japan Science and Technology Agency (Advanced Low Carbon Technology Research and Development Program). NMR measurements were conducted in JAIST, supported by Nanotechnology Platform Program (Molecule and Material Synthesis) of the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan. The authors would like to thank Prof. Dr. S. Ohki and Dr. A. Miyazawa in JAIST for technical assistance with the NMR measurements.
Author contributions
M.Y. proposed and supervised the project. M.Y. and O.S. designed the experiments. M.Y., Y.K. and Y.O. performed the experiments. M.T., M.W. and S.K. conducted thermodynamic consideration. All authors discussed the results. M.Y. wrote the manuscript.

Competing interests
The authors declare no competing interests.

Additional information
Supplementary information is available for this paper at https://doi.org/10.1038/s41598-019-51156-2.

Correspondence and requests for materials should be addressed to M.Y.

Reprints and permissions information is available at www.nature.com/reprints.

Publisher's note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

Open Access This article is licensed under a Creative Commons Attribution 4.0 International License, which permits use, sharing, adaptation, distribution and reproduction in any medium or format, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in a credit line to the material. If material is not included in the article’s Creative Commons license and your intended use is not permitted by statutory regulation or exceeds the permitted use, you will need to obtain permission directly from the copyright holder. To view a copy of this license, visit http://creativecommons.org/licenses/by/4.0/.

© The Author(s) 2019