

Probing the transformation paths from aluminum (oxy)hydroxides (boehmite, bayerite, and gibbsite) to metastable alumina: A view from high-resolution ^{27}Al MAS NMR

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ABSTRACT

Detailed knowledge of the structural evolution of diverse aluminum (oxy)hydroxides with varying temperatures up to $\sim 300^\circ\text{C}$ provides insights into the dehydration processes involving transitions among metastable phases on Earth's surface and in the crust. Here, we report the high-resolution solid-state ^{27}Al NMR spectra for three different types of aluminum (oxy)hydroxides (i.e., boehmite, bayerite, and gibbsite) with varying annealing temperatures up to 300°C , revealing the effect of distinct precursor minerals on the stability of metastable alumina. ^{27}Al MAS NMR results allow us to obtain the quantitative fractions and NMR parameters for each phase during transformation. The results demonstrate that each aluminum (oxy)hydroxide phase follows a unique transformation path to metastable alumina. The ^{27}Al MAS and 3QMAS NMR spectra of boehmite show that a minor but observable ^{41}Al signal ($\sim 2\%$) is detected at $\sim 50^\circ\text{C}$, and the ^{41}Al fraction gradually increases up to 300°C ($\sim 16\%$), indicating that the phase transformation from boehmite to $\gamma/\eta\text{-Al}_2\text{O}_3$ occurs at a temperature as low as $\sim 50^\circ\text{C}$, significantly lower than earlier estimations based on XRD. Together with the ^{41}Al fraction, the ^{51}Al fraction increases from $<1\%$ at 50°C to $\sim 2.3\%$ at 300°C , whereas the NMR results of bayerite and gibbsite do not show the presence of ^{51}Al . In addition, the ^{27}Al 3QMAS NMR spectra resolved the ^{61}Al site in boehmite and that in $\gamma/\eta\text{-Al}_2\text{O}_3$, which could not be uniquely determined from 1D NMR spectra. The population of bayerite abruptly decreases from 100% (at 150°C), through $\sim 47\%$ (at 200°C), to 0% (at 250°C), indicating that the phase transition from bayerite to boehmite + $\gamma/\eta\text{-Al}_2\text{O}_3$ occurs within a narrow temperature range. As for gibbsite, while ^{41}Al is not observed in the spectra up to 200°C , the ^{41}Al fraction of $\sim 2\%$ is observed in the spectra for gibbsite annealed at 250°C , and the ^{41}Al fraction increases rapidly to $\sim 15\%$ as the annealing temperature increases to 300°C , suggesting that the phase transformation into $\gamma/\eta\text{-Al}_2\text{O}_3$ occurs at $\sim 250^\circ\text{C}$. The results confirm that the phase transformation paths (gradual vs. dramatic) depend on the type of precursor minerals. Particularly, the onset temperature of the phase transformation from boehmite to metastable alumina ($\sim 50^\circ\text{C}$) is lower than those from other precursor minerals ($>150^\circ\text{C}$). Furthermore, the phase transformation from boehmite to $\gamma/\eta\text{-Al}_2\text{O}_3$ occurs gradually within broad temperature ranges from $\sim 50^\circ\text{C}$. This is due to their configurational disorder as evidenced by the presence of ^{51}Al . The observed structural evolution in aluminum (oxy)hydroxides in the low-temperature range facilitates our understanding of the nature of phase transformation and dehydration of oxides and hydroxides in the Earth's surface environments.

Keywords: Metastable (transition) alumina, aluminum (oxy)hydroxide, solid-state NMR, $\gamma/\eta\text{-Al}_2\text{O}_3$, phase transformation, extent of disorder

INTRODUCTION

The aluminum (oxy)hydroxides and aluminum oxides (i.e., alumina) exist in various stable and metastable polymorphs in the Earth's surface environments. Particularly, bauxite, which is the primary ore source of aluminum, consists of diverse types of aluminum (oxy)hydroxides, such as boehmite and gibbsite (e.g., Klopogge et al. 2006; Radusinović et al. 2017 and references therein). In addition, the various forms of metastable aluminum (oxy)hydroxides [e.g., pseudoboehmite and amorphous $\text{Al}(\text{OH})_3$] are found in the precipitates in acid mine drainage (e.g., Jones

et al. 2011; Kim 2015). The dehydration (and dehydroxylation) of aluminum (oxy)hydroxides (i.e., gibbsite and boehmite) in natural bauxite occurs at $200\text{--}300^\circ\text{C}$ (e.g., Klopogge et al. 2002), which corresponds to the temperature range of diagenesis. Although it is difficult to identify the metastable Al_2O_3 in natural bauxite due to their poor crystallinity, earlier studies have reported the presence of $\eta\text{-Al}_2\text{O}_3$ and hydrated- Al_2O_3 [i.e., akdalaite ($5\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$)] in natural bauxite (e.g., Tilley and Eggleton 1996; Hwang et al. 2006).

Aluminum oxides also exist in diverse metastable polymorphs, called transition alumina (such as γ -, δ -, θ -, κ -, χ -, and $\eta\text{-Al}_2\text{O}_3$), and stable $\alpha\text{-Al}_2\text{O}_3$. Metastable aluminas have diverse industrial applications such as catalyst supports, absorbents, and protective barriers to prevent corrosion on alumina-forming

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alloys because of their high surface area and the high catalytic activity at their surfaces (e.g., Che and Bennett 1989; Cai et al. 2003 and references therein). Extensive experimental and theoretical studies have revealed the structures and catalytic properties of metastable aluminas (e.g., John et al. 1983; Krokidis et al. 2001; Sohlberg et al. 2001; Cai et al. 2002; Paglia et al. 2003, 2006; Alphonse and Courty 2005; Kwak et al. 2008; Boumaza et al. 2009; Kim and Lee 2013b). Metastable aluminas can be obtained by the heat treatments of various aluminum (oxy)hydroxides precursors, such as boehmite (γ -AlOOH), bayerite [α -Al(OH) $_3$], and gibbsite [γ -Al(OH) $_3$]. Figure 1 shows the crystal structures for three different types of aluminum (oxy)hydroxides and γ -Al $_2$ O $_3$. The crystallographic information of aluminum (oxy)hydroxide precursors (i.e., boehmite, bayerite, and gibbsite) and metastable alumina (i.e., γ - and η -Al $_2$ O $_3$) are shown in Table 1 (Hill 1981; Balan et al. 2006, 2008).

The phase transformation paths from aluminum (oxy)hydroxides to stable α -Al $_2$ O $_3$ via metastable aluminas have been extensively explored (e.g., Levin and Brandon 1998; Digne et al. 2002; Chandran et al. 2019 and references therein). The transformation temperatures are also affected by various factors such as particle

size (Ingram-Jones et al. 1996; Tsukada et al. 1999; Bokhimi et al. 2007; Kim and Lee 2013b), morphology (Lee et al. 2015; Karouia et al. 2016), and synthesis conditions (Kim et al. 2005; Chen et al. 2018). Briefly, the annealing of boehmite (γ -AlOOH) produces the series of metastable alumina of γ -Al $_2$ O $_3$ (~300–500 °C), δ -Al $_2$ O $_3$ (~700–800 °C), and θ -Al $_2$ O $_3$ (900–1000 °C), and then stable α -Al $_2$ O $_3$ (1000–1100 °C) (e.g., Levin and Brandon 1998; Chagas et al. 2014). Bayerite [α -Al(OH) $_3$] transforms into α -Al $_2$ O $_3$ via η -Al $_2$ O $_3$ (200–300 °C) and θ -Al $_2$ O $_3$ (600–800 °C), or via boehmite (~150 °C), γ -Al $_2$ O $_3$ (300–450 °C), δ -Al $_2$ O $_3$ (~700–800 °C), and θ -Al $_2$ O $_3$ (900–1000 °C) (e.g., Pecharroman et al. 1999; Digne et al. 2002). The transformation to boehmite from bayerite is reported to occur above 150 °C with a fast heating rate (above 2 °C/min) (e.g., Maruthiprasad et al. 1988; Kim et al. 2005). As for gibbsite [γ -Al(OH) $_3$], the transformation sequence follows two paths depending on the particle size and water contents (e.g., Rouquerol et al. 1975; Mercury et al. 2006). Coarse gibbsite (i.e., > ~10 μ m), with excess water content generally transforms to boehmite at ~200 °C (Ingram-Jones et al. 1996; Hill et al. 2007; Chen et al. 2018). The annealing of fine gibbsite (~0.5 μ m) under a dry condition follows the sequence of χ -Al $_2$ O $_3$

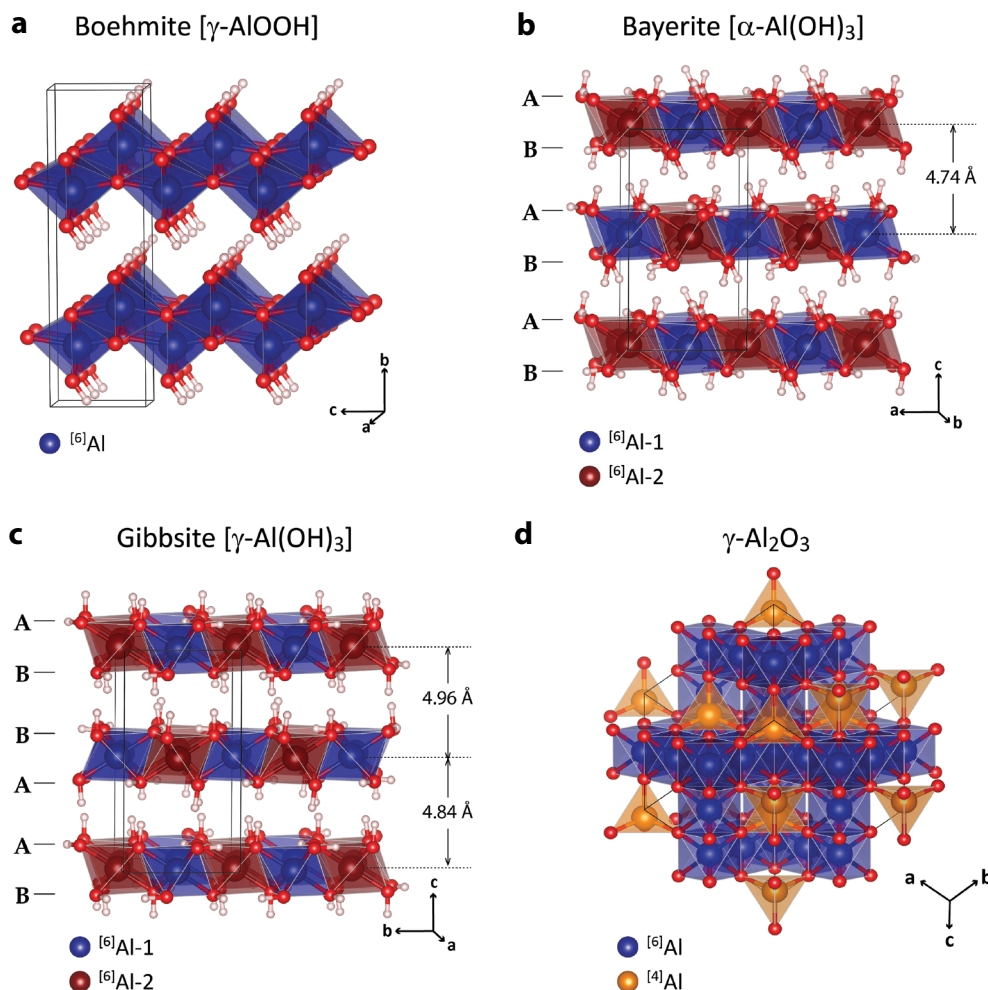


FIGURE 1. Crystal structures of (a) boehmite, (b) bayerite, (c) gibbsite, and (d) γ -Al $_2$ O $_3$. See Table 1 for details of crystal structures. (Color online.)

TABLE 1. Crystallographic information of aluminum (oxy)hydroxide precursor minerals (i.e., boehmite, bayerite, and gibbsite) and metastable alumina (i.e., γ -Al₂O₃ and η -Al₂O₃)

	Boehmite	Bayerite	Gibbsite
Al coordination	^[6] Al-1 100%	^[6] Al-1 50% ^[6] Al-2 50%	^[6] Al-1 50% ^[6] Al-2 50%
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>Cmcm</i>	<i>P2₁/m</i>	<i>P2₁/m</i>
Lattice parameter (Å)			
<i>a</i>	2.8796	5.096	8.742
<i>b</i>	12.205	8.729	5.112
<i>c</i>	3.761	9.489	9.801
Density (g/cm ³)	3.04	2.42	2.38–2.42
Reference	Hill (1981)	Balan et al. (2008)	Balan et al. (2006)
	γ -Al ₂ O ₃		η -Al ₂ O ₃
Crystal system	Cubic (defect spinel)		Cubic (defect spinel)
Space group	<i>Fd3m</i>		<i>Fd3m</i>
Lattice parameter (Å)			
<i>a</i>	7.911		7.914
Idealized formula	^[4] Al _{2/3} □ _{1/3} ^[6] Al ₂ O ₄		^[4] Al□ _{1/3} ^[6] Al _{5/3} O ⁴
^[4] Al: ^[6] Al	1:3 (~25:75)		3:5 (~38:62)
Reference	Lippens and De Boer (1964)		Zhou and Snyder (1991)

(150–300 °C), κ -Al₂O₃ (650–750 °C), and α -Al₂O₃ (~1000 °C) (Brindley and Choe 1961; Ingram-Jones et al. 1996). The phase transformation occurs over a broad temperature range rather than at a well-defined single temperature due to the pronounced metastability (see Levin and Brandon 1998; Kim and Lee 2013b; Chandran et al. 2019 and references therein). Furthermore, the metastability results in the coexistence of two or more phases at the same temperature.

Diverse experimental techniques such as differential thermal analysis (DTA), infrared (IR) spectroscopy, X-ray diffraction (XRD), and solid-state nuclear magnetic resonance (NMR) have observed phase transformations from aluminum (oxy) hydroxides into metastable aluminas (e.g., Bastow et al. 1994; Tsukada et al. 1999; Alphonse and Courty 2005; Karouia et al. 2016; Chen et al. 2018; Chandran et al. 2019). In particular, ²⁷Al NMR has revealed the Al coordination environments in diverse disordered crystalline (i.e., metastable)/amorphous Al₂O₃ and Al-(oxy)hydroxides (e.g., Lippmaa et al. 1986; Boissiere et al. 2006; Shen et al. 2007; Lee et al. 2003, 2009b, 2010; Sabarinathan et al. 2010; Kim and Lee 2013b; Cui et al. 2018; Lee and Ryu

2018; He et al. 2019 and references therein). The Al coordination environments and the NMR parameters, including quadrupolar coupling constant (*C_q*), isotropic chemical shifts (δ_{iso}), and asymmetry parameter (η) for aluminum (oxy)hydroxides and metastable aluminas from these earlier studies are summarized in Table 2. Whereas a presence of a small amount of metastable alumina is often difficult to identify via XRD, earlier ²⁷Al NMR results enable quantification of the fractions of coexisting phases in the transition aluminas and aluminum (oxy)hydroxides from the simulation of NMR spectra, even though the fraction of the minor phase is very small (Pecharroman et al. 1999; O'Dell et al. 2007; Kwak et al. 2008; Kim and Lee 2013b; Chagas et al. 2014; Chandran et al. 2019). We also show that the particle size and structural disorder in metastable alumina nanoparticles significantly affects their thermal stability above 600 °C (Kim and Lee 2013b).

Despite the geochemical implications and industrial applications, the precise determination of the short-range structure and stability (e.g., temperature conditions) of metastable aluminas in the low-temperature range (<300 °C) remains challenging. Par-

TABLE 2. ²⁷Al NMR parameters for aluminum (oxy)hydroxides and metastable alumina

Reference	Method	Phase	Larmor frequency (MHz)	^[6] Al	δ_{iso} (ppm) ^a	$\Delta\delta_{iso}$ ^b	<i>C_q</i> (MHz) ^c	η ^d	Site fraction (%)
Damodaran et al. (2002)	MQMAS	Boehmite	130.3	^[6] Al	12.6	–	1.8–2.8	0.5–1.0	100
		Bayerite		^[6] Al-1	9.1	–	1.9 ± 0.1	0.25 ± 0.05	50
				^[6] Al-2	13.1	–	1.4 ± 0.1	0.80 ± 0.05	50
		Gibbsite		^[6] Al-1	11.6	–	2.2 ± 0.2	0.75 ± 0.05	50
Vyalikh et al. (2010)	MAS	Gibbsite	130.3	^[6] Al-2	17.2	–	4.7 ± 0.2	1.00 ± 0.05	50
				^[6] Al-1	11.3 ± 0.2	–	2.2 ± 0.2	0.7 ± 0.1	50 ± 5
				^[6] Al-2	13.6 ± 0.2	–	4.6 ± 0.2	0.4 ± 0.1	50 ± 5
				^[6] Al	11.7–12.4	–	2.1–2.3	0.5–0.7	100
Ferreira et al. (2011)	Theoretical Calculation	Boehmite	–	^[6] Al	14.0 ± 1.0	6.5 ± 2.5	4.6 ± 1.0	–	68 ± 3
				^[4] Al	72.5 ± 1.0	10 ± 3	5.7 ± 1.0	–	32 ± 3
Kim and Lee (2013)	MAS (Czjzek)	γ -Al ₂ O ₃	130.3	^[6] Al	13.8	–	–	–	67
				^[4] Al	73.8	–	–	–	33
de Lacaillerie et al. (2008)	MAS (Czjzek)	γ -Al ₂ O ₃	130.3	^[6] Al	9 ± 1	–	4.5 ± 0.5	0.3	–
				^[4] Al	67 ± 1	–	5.0 ± 0.5	0.3	–
Kraus et al. (1996)	MAS	γ -Al ₂ O ₃	130.3	^[6] Al	14.5 ± 0.2	–	3.9 ± 0.2	0.4 ± 0.1	69–78
				^[4] Al	76.5 ± 0.2	–	4.5 ± 0.2	0.7 ± 0.1	22–31
Pecharroman et al. (1999)	MAS	η -Al ₂ O ₃	104.3	^[6] Al	15.2 ± 0.2	–	3.7 ± 0.2	0.4 ± 0.1	69–76
				^[5] Al	–	–	–	–	3–6.5
				^[4] Al	78.5 ± 0.2	–	4.7 ± 0.2	0.7 ± 0.1	21–26
				^[6] Al	–	–	–	–	–

^a Isotropic chemical shift.

^b Full-width at half maximum of the distribution of the isotropic chemical shift in the Czjzek model.

^c Quadrupolar coupling constant.

^d Asymmetry parameter.

ticularly, the transformation temperatures at which the formation of metastable alumina from diverse aluminum (oxy)hydroxides occurs remain to be determined. A systematic study of the changes in the Al coordination number with varying temperatures below 300 °C would, therefore, provide mechanistic details of the low-temperature surface processes. In this study, we investigated the dehydration paths to metastable alumina from various aluminum (oxy)hydroxide precursors (i.e., boehmite, bayerite, and gibbsite) in the low-temperature range up to 300 °C using high-resolution ^{27}Al MAS and 3QMAS NMR. We explored the effect of aluminum (oxy)hydroxide precursors (i.e., boehmite, bayerite, and gibbsite) on the stability of metastable alumina below 300 °C. Based on our spectroscopic results in the low-temperature range, we discuss the importance of the structural findings in understanding the geological (dehydration) processes involving metastable phase transformation on the Earth's surface environments.

MATERIALS AND METHODS

Sample preparation

Boehmite ($\gamma\text{-AlOOH}$) and bayerite ($\alpha\text{-Al(OH)}_3$) were synthesized by hydrolysis of aluminum tri-*sec*-butoxide (ASB, Sigma Aldrich, product no. 2269-22-9). The type of precursor synthesized depends on the amount of water used for hydrolysis of ASB (e.g., Serna et al. 1977; Vaudry et al. 1996). Particularly, boehmite is formed by the hydrolysis of ASB with $\text{H}_2\text{O}/\text{Al}$ of ~ 3 , while the hydrolysis with a higher amount of excess water (i.e., $\text{H}_2\text{O}/\text{Al} > 20$) results in the formation of bayerite. Boehmite was prepared by adding 4.52 g of aluminum tri-*sec*-butoxide to 1.04 mL of distilled water. The mixture was dried for a week at 25 °C in air. Bayerite was synthesized from a mixture of 5.23 g of aluminum tri-*sec*-butoxide with 200 mL of distilled water, which was dried at room temperature. Gibbsite [99.7% of $\gamma\text{-Al(OH)}_3$] was obtained from KC Corporation in Korea and was used as received. The median value of the particle size distribution (D_{50}) for as-received gibbsite is ~ 50 μm . The samples were annealed at varying temperatures in a vertical tube furnace from 110 to 300 °C and in a heating mantle up to 50 °C (2 h). The annealing temperature of the samples was increased with a rate of 275 °C/h to the target temperatures (e.g., 110–300 °C), and further isothermal annealing was performed for 2 h. Note that the total heating time (i.e., time to the elevated temperature + isothermal annealing time) slightly varies with the target temperature from 2.5 h for 110 °C to 3 h for 300 °C.

X-ray diffraction

X-ray diffraction patterns for starting materials (i.e., boehmite, bayerite, and gibbsite) and heat-treated samples were collected on Rigaku Miniflex 600 diffractometer using $\text{CuK}\alpha$ X-ray (a voltage of 40 kV and a current of 15 mA) with 2 θ range of 10–80°, step size of 0.02–0.04°, and a scan rate of 1–3 s per point.

NMR spectroscopy

^{27}Al MAS NMR spectra were obtained using a Bruker Avance II 500 MHz NMR system (11.7 T, at Seoul National University) with 4 mm triple-resonance MAS probe at Larmor frequency of 130.28 MHz. For a series of boehmite, ^{27}Al NMR spectra were also obtained with a Varian 600 spectrometer (14.1 T, at Korea Basic Science Institute) with 2.5 mm double-resonance probe at Larmor frequency of 156.34 MHz. Sample spinning speeds of 15 kHz (11.7 T) and 20 kHz (14.1 T) were used. A single-pulse sequence with ~ 0.2 μs ($\sim 15^\circ$ tip angle for central transition in solids) and delay time of 1 s were used. The baseline of the collected 1D NMR spectra was fitted by a fourth-order polynomial function using Topspin 3.5 software, and then, was subtracted from the obtained spectra for flattening the baseline around central transition peaks (~ 200 to ~ 200 ppm). The phase of each spectrum was carefully adjusted to optimize the baseline of the spectra. The simulation of ^{27}Al MAS NMR spectra was performed with the Dmfit program (Massiot et al. 2002). ^{27}Al 3QMAS NMR spectra were collected on the Varian 400 MHz (9.4 T) spectrometer with a Doty Scientific double-resonance MAS probe and a 4 mm thick-wall zirconia rotor. The fast amplitude modulation-based on shifted-echo pulse sequences comprising two hard pulses (with 3 and 0.7 μs) and a soft pulse (with 15 μs) were used. An echo-delay of ~ 0.5 ms (half-integer multiple of the rotor period) was used with a phase table of 96 cycles, designed

to select full echo. The pulse lengths used in the current sequence are carefully optimized to ensure maximum intensity. The radio-frequency (r_f) field strengths for hard pulses for ^{27}Al 3QMAS NMR are ~ 125 kHz. Approximately 120–200 FIDs (with the 192 number of scans) were collected to construct the 2D spectra. To achieve the current signal-to-noise ratio, ~ 16 h of collection time were required for each spectra. 3QMAS NMR spectra were processed with a shear transformation, with the isotropic dimension frequencies scaled as described previously (e.g., Baltisberger et al. 1996; Lee 2011; Kim and Lee 2014 and references therein). The recycle delay of 1 s and spinning speed of 15 kHz were used. All spectra were referenced to AlCl_3 (1 M) solution.

RESULTS AND DISCUSSION

Transformation from boehmite to γ -/ η - Al_2O_3

XRD results. Figure 2a shows the XRD patterns of boehmite with varying annealing temperatures up to 300 °C. The XRD pattern at 25 °C shows the broad diffraction peaks of boehmite, consistent with previous XRD studies (e.g., MacKenzie et al. 2000; Krokidis et al. 2001; Boumaza et al. 2009 and references therein). The diffraction patterns do not change much with annealing temperature up to 250 °C, suggesting that the transformation from boehmite to metastable Al_2O_3 at the range of 25–250 °C is not prevalent. In contrast, the pattern of boehmite annealed at 300 °C revealed the (400) and (440) peaks of metastable Al_2O_3 , indicating the presence of metastable Al_2O_3 (i.e., $\gamma\text{-Al}_2\text{O}_3$ and/or $\eta\text{-Al}_2\text{O}_3$).

Note that the XRD patterns of $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$ are almost identical (Lippens and De Boer 1964; Zhou and Snyder 1991). As shown in Table 1, both $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$ structures are described as defect spinel structures with space group $Fd\bar{3}m$ (e.g., Levin and Brandon 1998). The only difference stems from the variations in the distribution of vacancy in the cation sites: the vacancy in ideal $\gamma\text{-Al}_2\text{O}_3$ is located in the tetrahedral sites, while that in $\eta\text{-Al}_2\text{O}_3$ appears to favor octahedral sites (e.g., Lippens and De Boer 1964). As $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$ are not well-distinguished (e.g., Zhou and Snyder 1991), we refer to the metastable alumina as γ -/ η - Al_2O_3 . The width of the diffraction patterns of boehmite at 25 °C is broader than those of bayerite and gibbsite, indicating the low crystallinity and/or a more pronounced structural disorder in boehmite (see below).

^{27}Al NMR results. Figures 2b and 2c show the ^{27}Al MAS NMR spectra (11.7 and 14.1 T) for synthesized boehmite with varying annealing temperatures up to 300 °C. At 25 °C (as-synthesized boehmite), the spectrum predominantly shows ^{61}Al at ~ 10 ppm, consistent with previous NMR studies (Bastow et al. 1994; Isobe et al. 2003). However, a minor, $\sim 1\%$ of ^{41}Al peak at ~ 68 ppm is observed at 25 °C. As the ^{41}Al peak is not due to the rotor background (e.g., Lee et al. 2010, 2016), it may partly result from the presence of aluminum (oxy)hydroxide complex with ^{41}Al , such as Al_{13} [i.e., $\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_7^{12+}$] (e.g., Phillips et al. 2000a; Kim 2015). In addition, while the boehmite in the current study was not ground, the earlier studies have reported that the grinding of boehmite can result in the presence of ^{41}Al in boehmite (e.g., Chen et al. 1992; MacKenzie et al. 2000). Furthermore, the possible presence of a minor amount of γ -/ η - Al_2O_3 at ambient temperature may not be fully ruled out.

As the annealing temperature increases, the ^{41}Al peak intensity (at ~ 70 ppm) gradually increases. The ^{41}Al peak width also increases with increasing annealing temperature. Particularly, the peak width of ^{41}Al increases from ~ 16 ppm (for boehmite annealed at 50 °C) to ~ 22 ppm (for boehmite annealed at 300 °C)

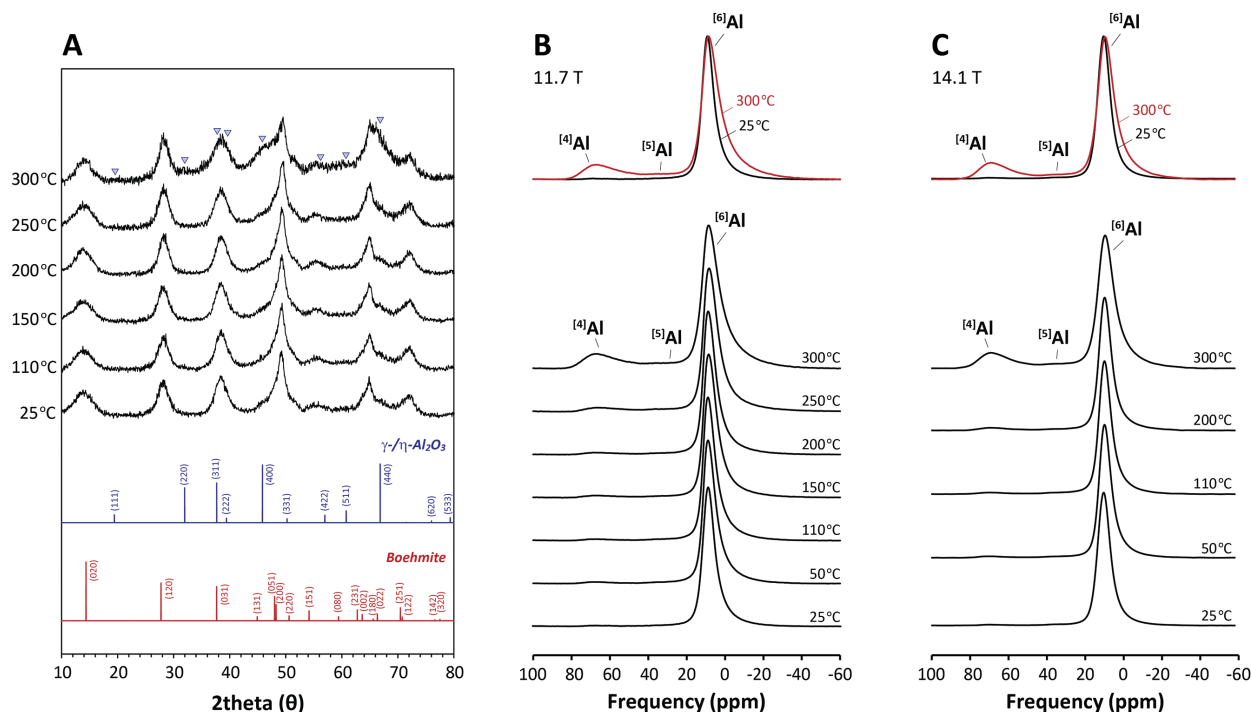


FIGURE 2. (a) XRD patterns for boehmite with varying annealing temperatures up to 300 °C. Red and blue vertical lines correspond to the peak positions and intensities of boehmite (JCPDS file no. 00-021-1307) and γ -/ η - Al_2O_3 (JCPDS file nos. 01-079-1558/00-21-0010), respectively. ^{27}Al MAS NMR spectra for boehmite with varying temperatures at 11.7 T (b) and 14.1 T (c). (Color online.)

at 11.7 T, and it increases from ~ 14 ppm (at 50 °C) to ~ 20 ppm (at 300 °C) at 14.1 T (see Fig. 3). The narrower peak widths of Al sites at 14.1 T (than those at 11.7 T) is because the magnitude of quadrupolar interaction decreases with increasing magnetic fields (e.g., Kohn et al. 1998; Stebbins et al. 2000 and references therein). The spectra at both fields reveal a small but noticeable presence of $^{[5]}\text{Al}$ (at ~ 35 ppm), and the fraction of $^{[5]}\text{Al}$ apparently increases with increasing annealing temperature. These results indicate that the phase transformation from boehmite to γ -/ η - Al_2O_3 occurs at a temperature as low as ~ 50 °C. The presence of small amounts of γ -/ η - Al_2O_3 below 300 °C, which was observed in high-resolution NMR spectra, is not revealed in the XRD pat-

terns. Note that, while ideal γ - Al_2O_3 and η - Al_2O_3 structures have different $^{[4]}\text{Al}$: $^{[6]}\text{Al}$ ratios, it is difficult to distinguish γ - Al_2O_3 and η - Al_2O_3 in the NMR spectra and these phases often coexist (Lippens and De Boer 1964; Damodaran et al. 2002; Digne et al. 2002; Chandran et al. 2019).

Transformation from bayerite to boehmite + γ -/ η - Al_2O_3

XRD results. Figure 4a shows the XRD patterns for bayerite with varying annealing temperatures up to 300 °C. The width of the main diffraction peaks [i.e., (002) peak] for bayerite at 25 °C ($\sim 0.2^\circ$) is significantly narrower than that for boehmite at 25 °C ($\sim 5^\circ$), indicating that the crystallinity of bayerite is

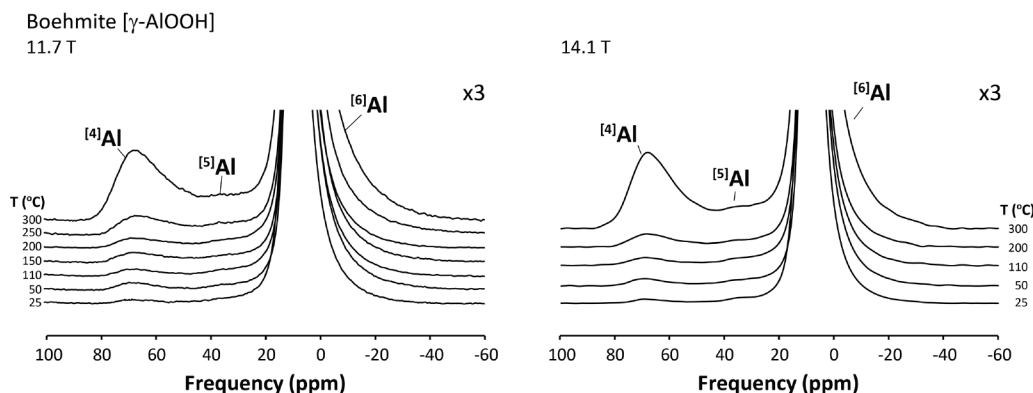


FIGURE 3. The enlarged ^{27}Al MAS NMR spectra for boehmite with varying annealing temperatures obtained at 11.7 T (left) and 14.1 T (right). (Color online.)

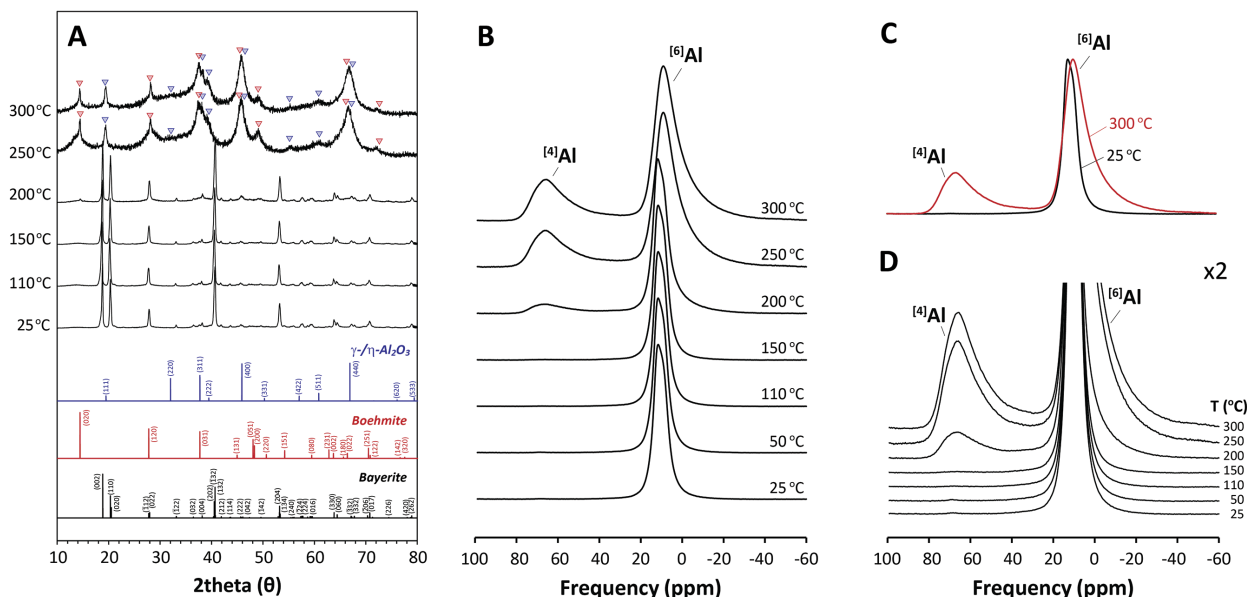


FIGURE 4. (a) XRD patterns for bayerite with varying annealing temperatures up to 300 °C. Black, red, and blue vertical lines correspond to the peak positions and intensities of bayerite (JCPDS file no. 01-083-2256), boehmite (JCPDS file no. 00-021-1307), and γ -/ η -Al₂O₃ (JCPDS file no. 00-21-0010), respectively. (b) ²⁷Al MAS NMR spectra at 11.7 T for bayerite with varying temperatures. (c) Comparison of ²⁷Al NMR spectra for bayerite at 25 °C (black line) and 300 °C (red line). The enlarged ²⁷Al NMR spectra (d) are also shown to manifest the evolution of [4]Al sites. (Color online.)

higher than that of boehmite. As shown in Figure 4a, there are no significant changes in the XRD patterns with increasing the annealing temperature for bayerite up to 200 °C. However, for the bayerite annealed at 250 °C, the diffraction patterns of bayerite abruptly disappear. Instead, patterns of both boehmite and metastable alumina are observed. The XRD results confirm that the bayerite transformed into boehmite and metastable Al₂O₃ (i.e., γ -/ η -Al₂O₃) above ~250 °C, consistent with previous studies (Zhou and Snyder 1991; Digne et al. 2002).

²⁷Al NMR results. Figures 4b–4d present the ²⁷Al MAS NMR spectra at 11.7 T of bayerite with varying annealing temperatures up to 300 °C, showing the evolution of Al sites due to the phase transformation of bayerite to boehmite + metastable γ -/ η -Al₂O₃. For the spectra of bayerite at 25 °C, the asymmetric shape of [6]Al peak (with the peak maximum at ~11.4 ppm) is observed. The [6]Al peak shape with a shoulder at ~8 ppm may be due to two crystallographic inequivalent [6]Al sites, consistent with the previous NMR study (Bastow et al. 1994). The previously reported NMR parameters for bayerite are shown in Table 2 (Damodaran et al. 2002). As shown in Figure 4b, only [6]Al peak is observed in the spectra for annealed bayerite up to 150 °C. A noticeable fraction of [4]Al sites is observed in the spectra for bayerite annealed at 200 °C, and the fraction of [4]Al increases with increasing temperature from 200 to 300 °C. Though the difference is minor, the [6]Al peak width increases with increasing temperature from ~7 ppm (at 150 °C) to ~8 ppm (at 200 °C), suggesting the increase in the fraction of disordered phase (i.e., metastable alumina) with increasing temperature. In addition, the peak shape evolves with long tails extending the lower-frequency range due to a larger extent of distribution of C_q above 200 °C. These results indicate that the phase transformation from bayerite to γ -/ η -Al₂O₃ occurs at ~200 °C. We also

note that the presence of γ -/ η -Al₂O₃ is not observed in the XRD pattern at 200 °C (Fig. 4a). The [5]Al sites are not observed in the spectra of the bayerite series, even at 300 °C (Fig. 4c), in contrast to the results of the boehmite series. Furthermore, the peak widths of [4]Al and [6]Al of the spectra of the phases formed from bayerite at 300 °C appear to be wider than those formed from the boehmite precursor at 300 °C (Fig. 2b), suggesting a larger fraction of metastable alumina in the former (see below for the quantification of phases).

Transformation from gibbsite to boehmite + γ -/ η -Al₂O₃

XRD results. In the XRD patterns of the gibbsite series (Fig. 5a), it is observed that the phase transformation from gibbsite to boehmite with increasing temperature occurs from ~200 °C. The intensity of the XRD pattern for boehmite gradually increases with increasing temperature from 200 to 300 °C. The XRD pattern for the gibbsite annealed at 300 °C shows that gibbsite is completely transformed into boehmite. Note that the peak width of gibbsite-derived boehmite (at 200 °C) is narrower than that of annealed boehmite formed from sol-gel synthesis at 200 °C, suggesting the higher crystallinity in the former. Though minor, the broad diffraction peaks of metastable-Al₂O₃ (at the 2θ of ~37°, ~43°, and ~66°) are observed in the pattern of heat-treated gibbsite at 300 °C. However, for gibbsite annealed at 250 °C, the presence of γ -/ η -Al₂O₃ is not confirmed in the current XRD pattern.

²⁷Al NMR results. Figures 5b–5d show the ²⁷Al MAS NMR spectra at 11.7 T for gibbsite with varying annealing temperatures. The spectra at 25 °C show two crystallographically distinct [6]Al sites (Bastow et al. 1994; Hill et al. 2007). See Table 2 for detailed information on the previously reported NMR parameters for two different [6]Al sites. Above 200 °C, the spectra show subtle and

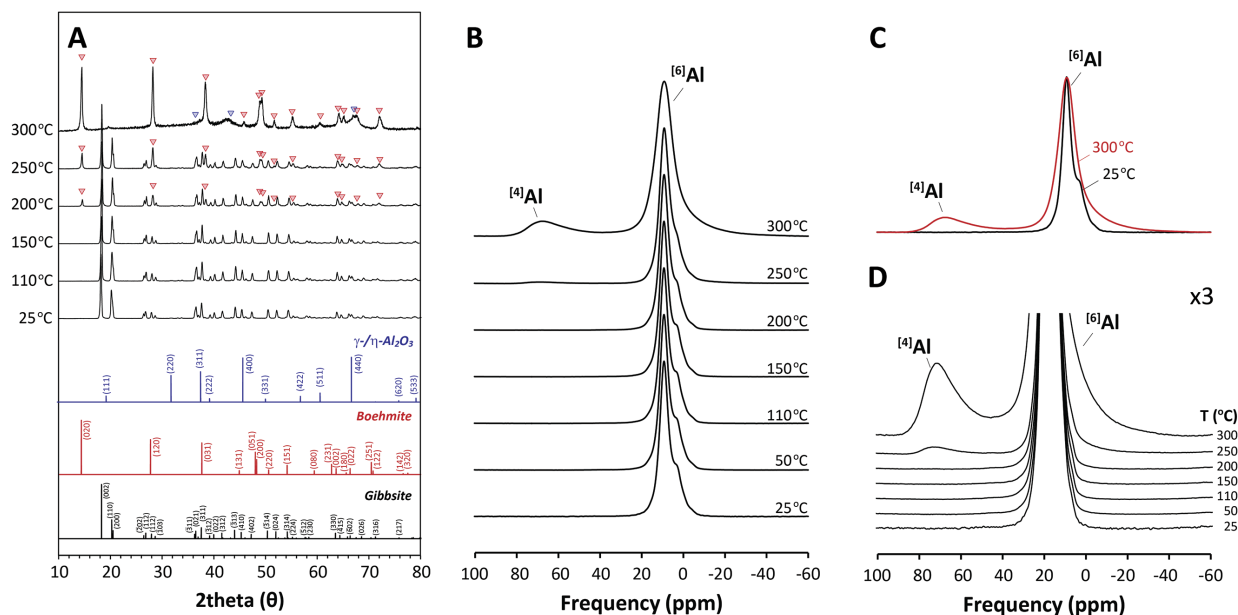


FIGURE 5. (a) XRD patterns for gibbsite with varying annealing temperatures up to 300 °C. Black, red, and blue vertical lines correspond to the peak positions and intensities of gibbsite (JCPDS file no. 01-070-2038), boehmite (JCPDS file no. 00-021-1307), and γ - η -Al₂O₃ (JCPDS file no. 01-079-1558), respectively. (b) ²⁷Al MAS NMR spectra at 11.7 T for gibbsite with varying temperatures. (c) Comparison of ²⁷Al NMR spectra for gibbsite at 25 °C (black line) and 300 °C (red line). The enlarged ²⁷Al NMR spectra (d) are also shown to manifest the evolution of [4]Al sites. (Color online.)

gradual changes in the peak shape of [6]Al, suggesting the phase transformation to boehmite. At 250 °C, the [4]Al peak is observed, and the peak intensity of [4]Al increases with increasing temperature (Fig. 5d). Although the presence of γ - η -Al₂O₃ at 250 °C is not observed in the XRD patterns, the presence of [4]Al peak in the NMR spectra at 250 °C confirms the formation of γ - η -Al₂O₃. This indicates that XRD alone may not reveal the presence of minor amount of structural disordered (or poorly crystalline) metastable Al₂O₃ phases. The [5]Al peak in the heat-treated gibbsite is not evident in the NMR spectra, while the presence of [5]Al is observed in the heat-treated boehmite (see discussion below).

²⁷Al 3QMAS NMR results for boehmite with varying temperature

In addition to structural insights from 1D MAS NMR spectra (Figs. 2–5), 2D 3QMAS NMR spectra for the samples allow us to trace the detailed changes in the populations of phases involving transformation. Figure 6 shows the ²⁷Al 3QMAS NMR spectra for boehmite before and after annealing at 110, 200, and 300 °C for 2 h, providing enhanced resolution among Al sites. By achieving the current signal-to-noise ratio, a minor fraction of [4,5]Al sites can be resolved in the current 2D NMR spectra. Note that the noise overlapping the signal of [n]Al was not observed on the 1% contour line (see Online Materials! OM1). In addition, the overlap between the signals and spinning sideband was not observed in the current spectra. The [6]Al peak at ~–10 ppm in the isotropic dimension is observed at 25 °C. As the temperature increases from 110 to 300 °C, the [5]Al peak at ~–28 ppm and [4]Al peak at ~–45 ppm in the isotropic dimension apparently increase (e.g., Baltisberger et al. 1996; Stebbins et al. 2000;

Lee et al. 2009b). The increase in the intensities of [4,5]Al sites indicates that phase transformation of boehmite → γ - η -Al₂O₃ occurs gradually within a broad temperature range. These results are consistent with those of the ²⁷Al MAS NMR spectra (Fig. 3).

Figure 7 shows the changes in [6]Al with increasing annealing temperature resulting from the variations in the relative fractions between boehmite and γ - η -Al₂O₃. The 2D NMR spectra resolved the [6]Al site in boehmite and that in γ - η -Al₂O₃, which could not be uniquely determined from 1D NMR spectra. The expected position of [6]Al peak in boehmite and γ - η -Al₂O₃ can be estimated from the NMR parameters shown in Table 2 (Kraus et al. 1996; Pecharroman et al. 1999; Perander et al. 2007; Kim and Lee 2013b) and currently estimated parameters from the simulation of ²⁷Al MAS NMR spectra (Table 3). These are marked in the ²⁷Al 3QMAS NMR spectra (Fig. 7) where the evolution of the shape of [6]Al peaks with varying annealing temperature are highlighted. These changes confirm that the onset of the phase transformation boehmite → γ - η -Al₂O₃ is evident at the temperature lower than the expected (<300 °C).

Quantification of coexisting phases in the heat-treated aluminum (oxy)hydroxides

Quantification protocols. Because the unique peak shapes of Al sites in aluminum (oxy)hydroxides and metastable alumina (due to their characteristic NMR parameters) allow us to deconvolute (and simulate) the NMR spectra, the fraction of constituent phases in the heat-treated samples was estimated from the NMR spectra (Figs. 8–10). To simulate the NMR spectra for highly ordered crystalline phases (i.e., bayerite and gibbsite), Q-mas 1/2 model in Dmfit software was used (e.g., Massiot et al. 2002; Lee et al.

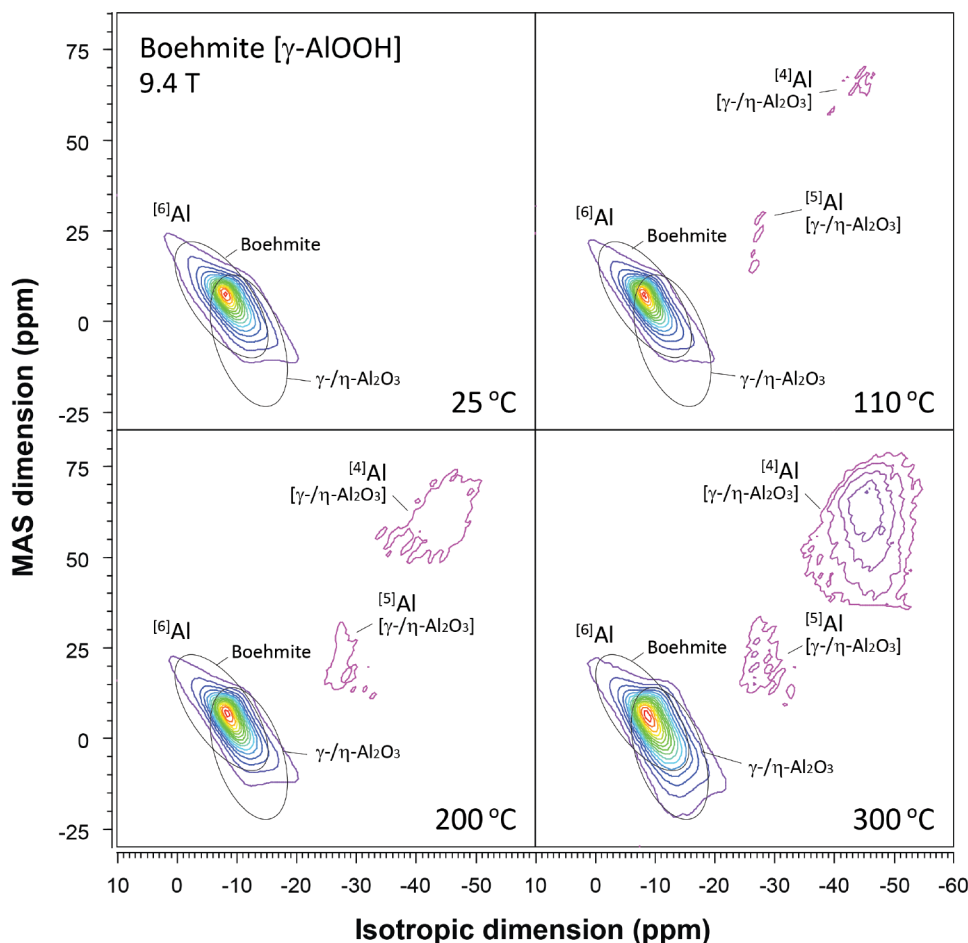


FIGURE 6. ^{27}Al 3QMAS NMR spectra for boehmite with varying annealing temperatures (as labeled) at 9.4 T. The contour lines are drawn from 8 to 98% relative intensity with a 6% increment. Four additional contour lines (1, 2.5, 4, and 6%) were added in $^{[4,5]}\text{Al}$ sites to better show low-intensity peaks (see Online Materials¹ OM1 for 2D spectra without noise removal). (Color online.)

2009a; Park and Lee 2019). In the current study, we simulated the bayerite and gibbsite using well-established values of NMR parameters previously obtained by 2D NMR. While the slight variation stems from the adjustment to match among experimental and simulated spectra, the NMR parameters were well-reproduced within the error range. The spectra for boehmite and metastable alumina were fitted (using DMFIT software) using a Gaussian isotropic model distribution (GIM, case of $d = 5$ of the more general Cjzek distribution), which assumes a statistical distribution of charges around the observed nuclei [see references Le Caer and Brand (1998), Neuville et al. (2004), Lee et al. (2009a), and Kim and Lee (2013b) for more detailed discussion on GIM and the detailed parameterization to simulate the quadrupolar line shape with disorder and thus the distribution of electronic field gradient tensors] (see Online Materials¹ OM2 for details of simulation using Dmfit).

In the current study, the following protocol has been used to estimate the population of aluminum (oxy)hydroxides and metastable alumina at varying temperatures. First, the ^{27}Al NMR spectra were simulated using the NMR parameters reported in the previous studies (Pecharroman et al. 1999; Damodaran et al. 2002; Vyalikh et al. 2010; see Table 2; Kim and Lee 2013b).

Then, these parameters are slightly adjusted to better reproduce the overall spectra. Second, the constraints on the relative ratio between Al sites for each phase were applied: boehmite is composed of a single disordered $^{[6]}\text{Al}$ site (Damodaran et al. 2002), and bayerite and gibbsite have two crystallographic inequivalent $^{[6]}\text{Al}$ sites with a ratio of 1:1 (Bastow et al. 1994; Damodaran et al. 2002; Vyalikh et al. 2010). For the ideal structures of $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$, the $^{[4]}\text{Al}$: $^{[6]}\text{Al}$ ratios are 25:75 and 38:62, respectively, as shown in Table 1 (John et al. 1983; Zhou and Snyder 1991). However, the ratio of $^{[4]}\text{Al}$ and $^{[6]}\text{Al}$ of $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$ of the defected cubic (spinel) structure varies depending on the distribution of defects on the Al sites (Levin and Brandon 1998). In addition, it is difficult to obtain pure $\gamma\text{-Al}_2\text{O}_3$ and/or $\eta\text{-Al}_2\text{O}_3$ phases from precursors (Lippens and De Boer 1964; Digne et al. 2002). Practically, the earlier NMR studies have shown that the $^{[4]}\text{Al}$ and $^{[6]}\text{Al}$ fractions in model $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$ are ~30% and ~70%, respectively (Pecharroman et al. 1999; Kim and Lee 2013b; Chandran et al. 2019). The reported $^{[4]}\text{Al}$ and $^{[6]}\text{Al}$ ratios are in between those for ideal structures of $\gamma\text{-Al}_2\text{O}_3$ (i.e., $^{[4]}\text{Al}$: $^{[6]}\text{Al}$ = 25:75) and/or $\eta\text{-Al}_2\text{O}_3$ (i.e., $^{[4]}\text{Al}$: $^{[6]}\text{Al}$ = 38:62). This suggests that $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$ often coexist. Thus, in the current study, the $^{[4]}\text{Al}$: $^{[6]}\text{Al}$ ratios for $\gamma\text{-}/\eta\text{-Al}_2\text{O}_3$ were constrained to be 3:7.

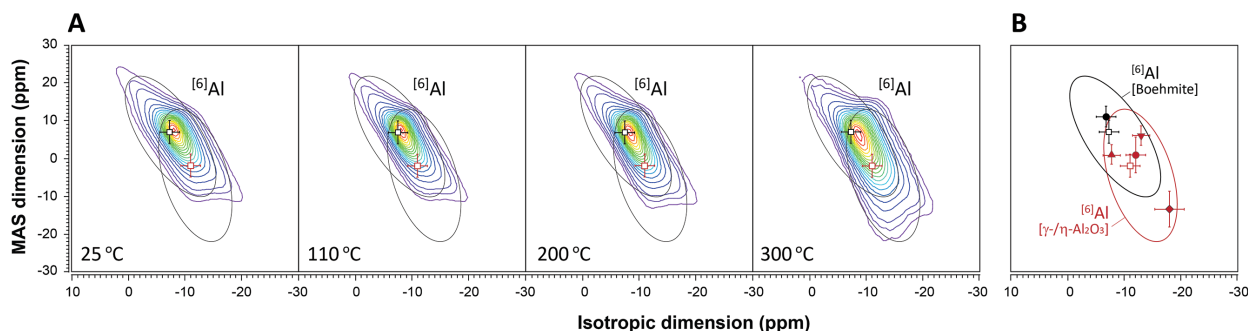


FIGURE 7. (a) ^{61}Al peaks in ^{27}Al 3QMAS NMR spectra for boehmite with varying annealing temperatures up to 300 °C. Contour lines are drawn from 8 to 98% of the relative intensity with increment of 5%. (b) Expected center of gravity for boehmite and $\gamma/\eta\text{-Al}_2\text{O}_3$ calculated on the basis of the current simulation (open symbols) and previous works [solid symbols, black circle (Damodaran et al. 2002); red triangle (Kraus et al. 1996); red inverted-triangle (Pecharroman et al. 1999); red diamond (Perander et al. 2007); red circle (Kim and Lee 2013)]. Black and red symbols refer to boehmite and $\gamma/\eta\text{-Al}_2\text{O}_3$, respectively. (Color online.)

With the constraint of the intensity ratio of ^{41}Al and ^{61}Al for $\gamma/\eta\text{-Al}_2\text{O}_3$, the fractions of precursors and the coexisting $\gamma/\eta\text{-Al}_2\text{O}_3$ were estimated (see below). As the presence of ^{41}Al is exclusively accompanied with the metastable alumina, the fractions of metastable alumina were obtained by the sum of ^{41}Al and the corresponding ^{61}Al (i.e., $X_{[61]\text{Al}}^{\gamma/\eta\text{-Al}_2\text{O}_3} = \frac{7}{3} \cdot X_{[41]\text{Al}}$). The remaining ^{61}Al intensity (e.g., total $X_{[61]\text{Al}} - \frac{7}{3} \cdot X_{[41]\text{Al}}$) is thus attributed to the fraction of aluminum (oxy)hydroxide precursors, because the

TABLE 3. ^{27}Al NMR parameters for the simulation of the NMR spectra for boehmite with varying temperatures at 11.7 and 14.1 T

Precursor mineral	T (°C)	Phase	^{61}Al	δ_{iso} (ppm) ^a	C_q (MHz) ^b	$\Delta\delta_{\text{iso}}^c$	^{61}Al fraction for each phase (%) ^{d,e}
Boehmite	25	Boehmite	^{61}Al	10.8 ± 1.5	2.7 ± 0.3	4 ± 2	99 ± 1
			^{41}Al	73.0 ± 1.5	5.0 ± 1.0	4 ± 2	<1
	50	Boehmite	^{61}Al	10.5 ± 1.5	2.8 ± 0.3	4 ± 2	93 ± 3
			^{61}Al	11.4 ± 1.5	4.8 ± 0.5	6 ± 2	4 ± 3
			^{51}Al	41.3 ± 1.5	5.7 ± 1.0	6 ± 2	<1
			^{51}Al	73.4 ± 1.5	5.1 ± 1.0	7 ± 2	2 ± 3
	110	Boehmite	^{61}Al	10.5 ± 1.5	2.8 ± 0.3	4 ± 2	92 ± 3
			^{61}Al	11.4 ± 1.5	4.8 ± 0.5	7 ± 2	5 ± 3
			^{51}Al	41.3 ± 1.5	5.7 ± 1.0	6 ± 2	<1
			^{41}Al	73.6 ± 1.5	5.3 ± 1.0	7 ± 2	2 ± 3
	150	Boehmite	^{61}Al	10.2 ± 1.5	2.8 ± 0.3	4 ± 2	87 ± 3
			^{61}Al	11.1 ± 1.5	4.8 ± 0.5	7 ± 2	8 ± 3
			^{51}Al	41.0 ± 1.5	6.0 ± 1.0	6 ± 2	<2
			^{41}Al	73.4 ± 1.5	5.6 ± 1.0	9 ± 2	3 ± 3
	200	Boehmite	^{61}Al	10.5 ± 1.5	2.8 ± 0.3	5 ± 2	85 ± 3
			^{61}Al	12.2 ± 1.5	4.8 ± 0.5	7 ± 2	9 ± 3
			^{51}Al	41.0 ± 1.5	6.0 ± 1.0	6 ± 2	<2
			^{41}Al	73.9 ± 1.5	5.7 ± 1.0	10 ± 2	4 ± 3
	250	Boehmite	^{61}Al	10.1 ± 1.5	2.8 ± 0.3	5 ± 2	78 ± 3
			^{61}Al	11.8 ± 1.5	4.8 ± 0.5	7 ± 2	14 ± 3
			^{51}Al	41.2 ± 1.5	6.0 ± 1.0	6 ± 2	<2
			^{41}Al	73.7 ± 1.5	5.7 ± 1.0	9 ± 2	6 ± 3
	300	Boehmite	^{61}Al	10.6 ± 1.5	2.8 ± 0.3	5 ± 2	45 ± 3
			^{61}Al	12.1 ± 1.5	4.8 ± 0.5	8 ± 2	36 ± 3
			^{51}Al	41.0 ± 1.5	6.0 ± 1.0	7 ± 2	<3
			^{41}Al	73.9 ± 1.5	5.7 ± 1.0	10 ± 2	16 ± 3

Note: The ^{27}Al NMR spectra for boehmite at 25, 50, 110, 200, and 300 °C were simulated simultaneously at 11.7 and 14.1 T.

^a Isotropic chemical shift.

^b Quadrupolar coupling constant.

^c Full-width at half maximum of the distribution of the isotropic chemical shift in the Czek model.

^d ^{61}Al fraction for each phase = ^{61}Al for each phase/total area under NMR spectra.

^e The uncertainties of each Al site fraction stem from the deviation between experimental and simulated spectra (~1.5%), the contribution from the adjusted NMR parameters (~1.5%), the contribution of spinning sidebands (~1.5%), and phasing of the NMR spectrum (~1.5%). Considering these uncertainties, the total error bar of $\pm 3\%$ is estimated.

NMR peak area directly represents the fraction of phase: for example, the boehmite annealed at 300 °C contains $16 \pm 3\%$, $3 \pm 3\%$, and $36 \pm 3\%$ of ^{41}Al , ^{51}Al , and ^{61}Al for $\gamma/\eta\text{-Al}_2\text{O}_3$, respectively, indicating that there are ~55% of $\gamma/\eta\text{-Al}_2\text{O}_3$ and ~45% of boehmite in the sample. The NMR parameters were allowed to vary slightly, depending on the annealing temperature. The estimated NMR parameters and the fractions for Al sites of each phase at varying annealing temperatures were shown in Tables 3–5. Note that the fraction of ^{61}Al site for each phase shown in Tables 3–5 was obtained by calculating the ratio of the area under the ^{61}Al for the specific phase to the total area in the ^{27}Al MAS NMR spectra. The current NMR spectra were also simulated by considering the intensity of spinning sideband stemming from the satellite transition (see Online Materials¹ OM3 for details). Taking into consideration the minor difference in the estimated fractions of each phase at a given temperature between simulation results with considering and without considering the spinning sidebands (~1.5%), the contribution of satellite transition to quantification of the relative fraction between Al sites is minor.

Phase transformation from boehmite precursor. Figures 8 and 9 show the simulated ^{27}Al MAS NMR spectra at 11.7 and 14.1 T using identical NMR parameters. Despite the overlap, the ^{61}Al peak for $\gamma/\eta\text{-Al}_2\text{O}_3$ and that from boehmite can be partly distinguished. This is because of the higher C_q for ^{61}Al of $\gamma/\eta\text{-Al}_2\text{O}_3$ (~4.8 MHz) than that of boehmite (~2.7 MHz). Note that the reported C_q values for ^{61}Al of boehmite vary from 1.8 to 2.8 MHz (Damodaran et al. 2002; Chandran et al. 2019). The δ_{iso} of boehmite in the current study (~10.8 ppm) is somewhat different from that reported previously (~12.6 ppm) (Damodaran et al. 2002). This is because the NMR parameters in the current study were obtained by simulation of 1D NMR spectra using Czek model. In contrast, those in the previous study were obtained from the center of gravity of peak in the 2D NMR spectra (Damodaran et al. 2002). A minor ^{41}Al signal (~2%) is detected at a temperature as low as ~50 °C. The ^{41}Al fraction gradually increases from ~2% at 50 °C to ~4% at 200 °C, and then increases rapidly to ~7% and ~16% at 250 and 300 °C, respectively. The ^{51}Al fraction also increases from <1% at 50 °C to ~2.3% at 300 °C.

Phase transformation from bayerite precursor. Figure 10a shows the simulation results of the ^{27}Al MAS NMR spectra of bayerite heat-treated from 25 to 300 °C. Although the two crys-

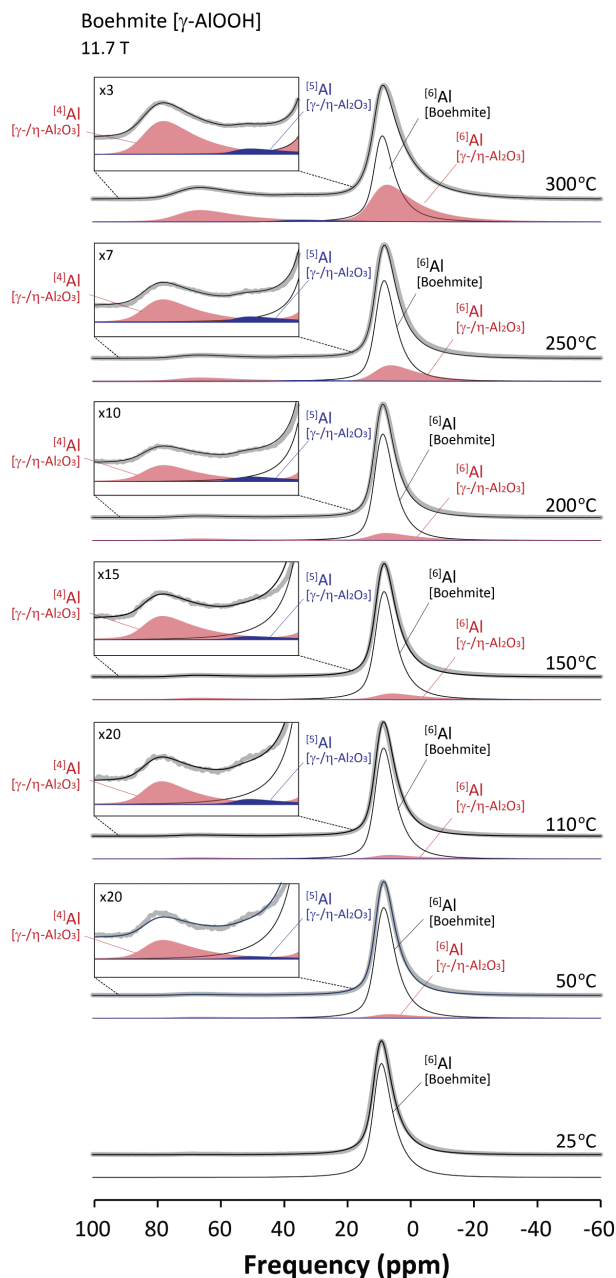


FIGURE 8. Simulation of ^{27}Al MAS NMR spectra obtained at 11.7 T for boehmite with varying annealing temperatures up to 300 °C. Thick gray lines refer to the experimental spectra, and thin black lines refer to the simulation results. Each component used in the simulation is shown as labeled. (Color online.)

tallographically inequivalent ^{6}Al sites in bayerite are not fully resolved in the 1D NMR spectra, the NMR parameters reported in earlier ^{27}Al NMR studies were used to deconvolute NMR spectra (Bastow et al. 1994; Damodaran et al. 2002): for example, as for bayerite, the δ_{iso} , C_q , and η values of ^{6}Al -1 are 9.8 ppm, 1.9 MHz, and 0.3, respectively, and those of ^{6}Al -2 are 12.9 ppm, 1.7 MHz, and 0.8, respectively (Table 4). As mentioned above (Fig. 4), the bayerite transforms into boehmite + γ - η - Al_2O_3 . Thus, the spectra were simulated above 200 °C using the multiple ^{4}Al and ^{6}Al

components corresponding to boehmite and γ - η - Al_2O_3 .

The simulation results show that there are ~14% of boehmite, ~39% of γ - η - Al_2O_3 , and ~47% of bayerite at 200 °C. The ^{4}Al fraction rapidly increases to ~25% as the annealing temperature increases up to 250 °C, and then gradually up to ~27% at 300 °C, confirming that the γ - η - Al_2O_3 (~91%) is predominant at 300 °C. This drastic increase in ^{4}Al fraction indicates that the phase transformation occurs dramatically within a narrow temperature range between 200 and 250 °C.

Phase transformation from gibbsite precursor. Figure 10b presents the simulation results for ^{27}Al MAS NMR spectra of gibbsite with varying annealing temperatures. The NMR spectra of gibbsite at 25 °C, showing the coexistence of two different ^{6}Al sites, were simulated with the two components. The ^{27}Al NMR parameters are $\delta_{\text{iso}} = 12.4$ ppm, $C_q = 4.5$ MHz, and $\eta = 0.4$ for the ^{6}Al -1 site and $\delta_{\text{iso}} = 11.3$ ppm, $C_q = 2.3$ MHz, and $\eta = 0.8$ for

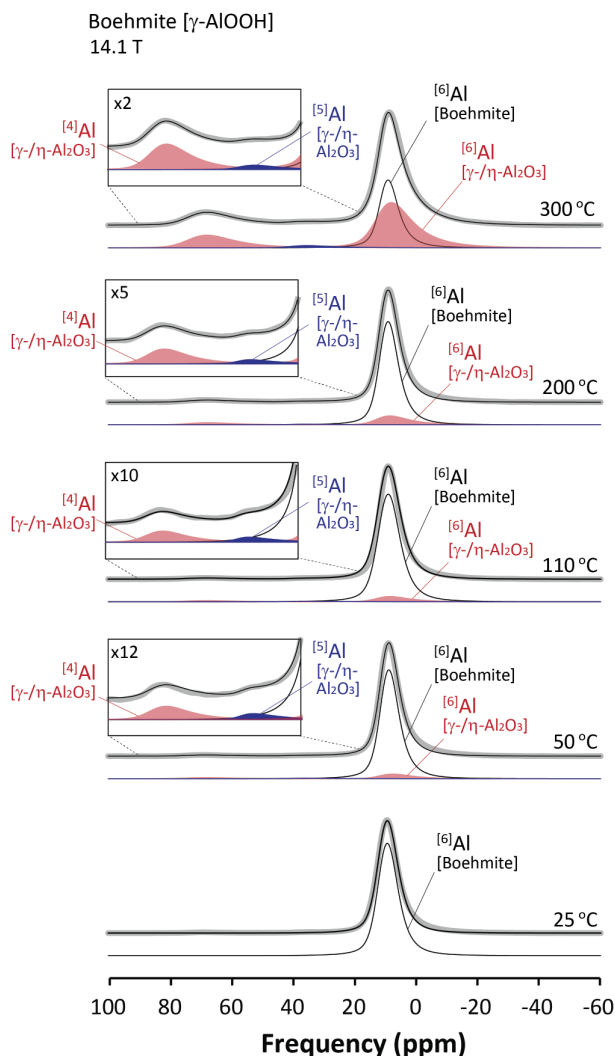


FIGURE 9. Simulation of ^{27}Al MAS NMR spectra obtained at 14.1 T for boehmite with varying annealing temperatures up to 300 °C. Thick gray lines refer to the experimental spectra, and thin black lines refer to the simulation results. Each component used in the simulation is shown as labeled. (Color online.)

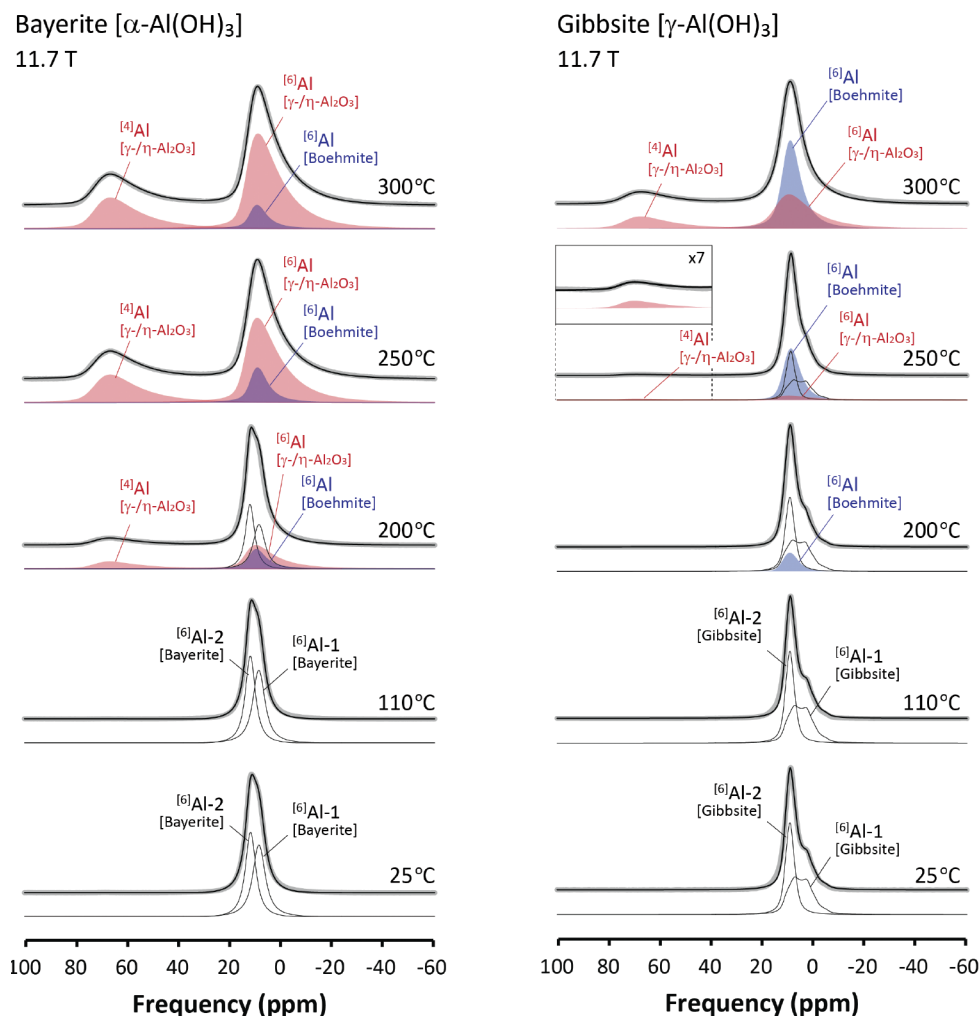


FIGURE 10. Simulation of ^{27}Al MAS NMR spectra obtained at 11.7 T for bayerite (left) and gibbsite (right) with varying annealing temperatures up to 300 °C. Thick gray lines refer to the experimental spectra, and thin black lines refer to the simulation results. Each component used in the simulation is shown as labeled. (Color online.)

the ^{6}Al -2 site (Table 5). These values are consistent with those obtained in the previous ^{27}Al MAS NMR study (Vyalikh et al. 2010). As the temperature increases above 200 °C, the peak shape of ^{6}Al changes gradually because the gibbsite starts to transform to boehmite. Note that the changes in ^{6}Al peak at 200 °C is not due to the formation of metastable alumina because the presence of ^{4}Al is not observed at 200 °C. Thus, the spectrum at 200 °C was simulated using a single ^{6}Al peak for boehmite and two ^{6}Al peaks for gibbsite. At 200 °C, the proportions of gibbsite and boehmite are ~88 and ~12%, respectively. Above 250 °C, the ^{4}Al fraction of γ - η - Al_2O_3 increases from ~2% at 250 °C to ~15% at 300 °C, suggesting that the phase transformation into γ - η - Al_2O_3 occurs at ~250 °C.

Temperature-induced changes in the population of Al-(oxy)hydroxides and metastable aluminas

Figure 11 shows the variations in the $^{4,5}\text{Al}$ fractions in aluminum (oxy)hydroxides and metastable alumina with varying

temperatures. At 25 °C, boehmite has ~1% of ^{4}Al , and bayerite and gibbsite do not have detectable ^{4}Al and ^{5}Al . The temperature at which the increase in $^{4,5}\text{Al}$ is first observed in the NMR spectra (i.e., the onset temperature of the phase transformation into metastable alumina) depends on the type of precursor hydroxide minerals. The presence of $^{4,5}\text{Al}$ peaks is observed in boehmite even at 50 °C (~2.7%), and the $^{4,5}\text{Al}$ fraction steadily increases up to 300 °C (~18%). In contrast, in the case of bayerite and gibbsite, the ^{4}Al peak intensity increases abruptly from 200 °C (~11%) to 250 °C (~26%), and then increases gradually from 250 to 300 °C (~27%). As for gibbsite, while the ^{4}Al fraction is not observed in the spectra up to 200 °C, the ^{4}Al fraction of ~2% is observed in the spectra for the 250 °C sample, and the ^{4}Al fraction increases rapidly to ~15% as the temperature increases to 300 °C.

Taking the temperature-induced changes in ^{4}Al fraction into consideration, Figure 12 exhibits the transformation paths from boehmite (12a), bayerite (12b), and gibbsite (12c) to γ - η - Al_2O_3 . As shown in Figure 12a, the fraction of γ - η - Al_2O_3 increases con-

TABLE 4. ^{27}Al NMR parameters for the simulation of the NMR spectra for bayerite with varying temperatures at 11.7 T

Precursor mineral	Larmor frequency (MHz)	T (°C)	Phase	$^{[n]}\text{Al}$	δ_{iso} (ppm) ^a	C_q (MHz) ^b	η^c	$\Delta\delta_{\text{iso}}^d$	$^{[n]}\text{Al}$ fraction for each phase (%) ^{e,f}
Bayerite	130.28	25	Bayerite	$^{[6]}\text{Al-1}$	9.8 ± 0.5	1.9 ± 0.3	0.3 ± 0.1	–	51 ± 3
				$^{[6]}\text{Al-2}$	12.9 ± 0.5	1.7 ± 0.3	0.8 ± 0.1	–	49 ± 3
		110	Bayerite	$^{[6]}\text{Al-1}$	9.8 ± 0.5	1.9 ± 0.3	0.3 ± 0.1	–	50 ± 3
				$^{[6]}\text{Al-2}$	13.0 ± 0.5	1.7 ± 0.3	0.8 ± 0.1	–	50 ± 3
		150	Bayerite	$^{[6]}\text{Al-1}$	9.8 ± 0.5	2.0 ± 0.3	0.3 ± 0.1	–	51 ± 3
				$^{[6]}\text{Al-2}$	12.9 ± 0.5	1.7 ± 0.3	0.8 ± 0.1	–	49 ± 3
		200	Bayerite	$^{[6]}\text{Al-1}$	9.9 ± 0.5	2.0 ± 0.3	0.3 ± 0.1	–	23 ± 3
				$^{[6]}\text{Al-2}$	13.1 ± 0.5	1.6 ± 0.3	0.8 ± 0.1	–	24 ± 3
		250	Boehmite	$^{[6]}\text{Al}$	11.2 ± 1.0	2.7 ± 0.5	–	4 ± 1	14 ± 3
				$^{[6]}\text{Al}$	13.5 ± 1.5	4.4 ± 0.5	–	5 ± 1	27 ± 3
			γ - η - Al_2O_3	$^{[4]}\text{Al}$	73.0 ± 1.5	5.4 ± 0.5	–	8 ± 1	12 ± 3
				$^{[6]}\text{Al}$	10.9 ± 1.5	2.7 ± 0.5	–	4 ± 1	14 ± 3
				$^{[6]}\text{Al}$	13.5 ± 1.5	4.8 ± 0.5	–	5 ± 1	60 ± 3
				$^{[4]}\text{Al}$	72.8 ± 1.5	5.4 ± 0.5	–	8 ± 1	26 ± 3
		300	Boehmite	$^{[6]}\text{Al}$	10.9 ± 1.5	2.7 ± 0.5	–	4 ± 1	9 ± 3
				$^{[6]}\text{Al}$	13.2 ± 1.5	4.8 ± 0.5	–	5 ± 1	64 ± 3
				$^{[4]}\text{Al}$	72.8 ± 1.5	5.4 ± 0.5	–	8 ± 1	27 ± 3

^a Isotropic chemical shift.^b Quadrupolar coupling constant.^c Asymmetry parameter.^d Full-width at half maximum of the distribution of the isotropic chemical shift in the Czejk model.^e $^{[n]}\text{Al}$ fraction for each phase = $^{[n]}\text{Al}$ for each phase/total area under NMR spectra.^f The uncertainties of each Al site fraction stem from the deviation between experimental and simulated spectra (~1.5%), the contribution from the adjusted NMR parameters (~1.5%), the contribution of spinning sidebands (~1.5%), and phasing of the NMR spectrum (~1.5%). Considering these uncertainties, the total error bar of $\pm 3\%$ is estimated.**TABLE 5.** ^{27}Al NMR parameters for the simulation of the NMR spectra for gibbsite with varying temperatures at 11.7 T

Precursor mineral	Larmor frequency (MHz)	T (°C)	Phase	$^{[n]}\text{Al}$	δ_{iso} (ppm) ^a	C_q (MHz) ^b	η^c	$\Delta\delta_{\text{iso}}^d$	$^{[n]}\text{Al}$ fraction for each phase (%) ^{e,f}
Gibbsite	130.28	25	Gibbsite	$^{[6]}\text{Al-1}$	12.4 ± 1.0	4.5 ± 0.3	0.4 ± 0.1	–	50 ± 3
				$^{[6]}\text{Al-2}$	11.3 ± 1.0	2.3 ± 0.3	0.8 ± 0.1	–	50 ± 3
		110	Gibbsite	$^{[6]}\text{Al-1}$	12.5 ± 1.0	4.5 ± 0.3	0.4 ± 0.1	–	50 ± 3
				$^{[6]}\text{Al-2}$	11.3 ± 1.0	2.3 ± 0.3	0.8 ± 0.1	–	50 ± 3
		150	Gibbsite	$^{[6]}\text{Al-1}$	12.5 ± 1.0	4.5 ± 0.3	0.4 ± 0.1	–	50 ± 3
				$^{[6]}\text{Al-2}$	11.3 ± 1.0	2.3 ± 0.3	0.8 ± 0.1	–	50 ± 3
		200	Gibbsite	$^{[6]}\text{Al-1}$	13.4 ± 1.0	4.6 ± 0.3	0.4 ± 0.1	–	44 ± 3
				$^{[6]}\text{Al-2}$	11.3 ± 1.0	2.3 ± 0.3	0.8 ± 0.1	–	44 ± 3
		250	Boehmite	$^{[6]}\text{Al}$	11.9 ± 1.5	2.5 ± 0.3	–	7 ± 1	12 ± 3
				$^{[6]}\text{Al-1}$	12.7 ± 1.0	4.5 ± 0.3	0.4 ± 0.1	–	23 ± 3
			γ - η - Al_2O_3	$^{[6]}\text{Al-2}$	11.2 ± 1.0	2.4 ± 0.3	0.8 ± 0.1	–	23 ± 3
				$^{[6]}\text{Al}$	10.6 ± 1.5	2.7 ± 0.3	–	5 ± 1	45 ± 3
				$^{[6]}\text{Al}$	14.0 ± 1.5	4.6 ± 0.5	–	6 ± 1	7 ± 2
				$^{[4]}\text{Al}$	73.2 ± 1.5	5.5 ± 0.5	–	7 ± 1	2 ± 1
		300	Boehmite	$^{[6]}\text{Al}$	10.6 ± 1.5	2.7 ± 0.3	–	5 ± 1	48 ± 3
				$^{[6]}\text{Al}$	13.8 ± 1.5	4.6 ± 0.5	–	8 ± 1	37 ± 3
				$^{[4]}\text{Al}$	73.9 ± 1.5	5.5 ± 0.5	–	9 ± 1	15 ± 3

^a Isotropic chemical shift.^b Quadrupolar coupling constant.^c Asymmetry parameter.^d Full-width at half maximum of the distribution of the isotropic chemical shift in the Czejk model.^e $^{[n]}\text{Al}$ fraction for each phase = $^{[n]}\text{Al}$ for each phase/total area under NMR spectra.^f The uncertainties of each Al site fraction stem from the deviation between experimental and simulated spectra (~1.5%), the contribution from the adjusted NMR parameters (~1.5%), the contribution of spinning sidebands (~1.5%), and phasing of the NMR spectrum (~1.5%). Considering these uncertainties, the total error bar of $\pm 3\%$ is estimated.

tinuously from ~8% at 50 °C to ~55% at 300 °C, suggesting that the phase transformation of boehmite $\rightarrow$ γ - η - Al_2O_3 occurs at a temperature as low as ~50 °C. The threshold temperature (~50 °C) is much lower than that previously reported. These results suggest that the phase transformation from boehmite to γ - η - Al_2O_3 occurs in a wide temperature range than previously reported. In contrast, as shown in Figure 12b, the population of bayerite abruptly decreases from 100% (at 150 °C), through ~47% (at 200 °C), to 0% (at 250 °C), indicating that the phase transition from bayerite to boehmite + γ - η - Al_2O_3 occurs within a narrow temperature range. Figure 12c shows the variations in the population among gibbsite, boehmite, and γ - η - Al_2O_3 with varying annealing temperatures. At 200 °C, the fraction of boehmite is ~12%. Above 250 °C, the fractions of both boehmite and γ - η - Al_2O_3 increase. In particular, the population of boehmite increases abruptly from ~12% to ~45% as the temperature increases from 200 to 250 °C, and then increases

gradually from ~45% at 250 °C to ~48% at 300 °C. The formation of γ - η - Al_2O_3 (~9%) is observed at 250 °C and the fraction of γ - η - Al_2O_3 increases dramatically from ~9% at 250 °C to ~52% at 300 °C. At 300 °C, the gibbsite is not observed. These results show that the threshold temperatures for gibbsite (~200 °C) are higher than that from boehmite (~50 °C).

Although further kinetic studies are certainly necessary (see below), the current NMR results confirm that the onset temperature and paths of transformation from aluminum (oxy)hydroxides to metastable alumina depend on the type of precursor minerals. In particular, the phase transformation of boehmite $\rightarrow$ γ - η - Al_2O_3 occurs at much lower temperatures (~50 °C) than those of bayerite $\rightarrow$ boehmite + γ - η - Al_2O_3 and gibbsite $\rightarrow$ boehmite + γ - η - Al_2O_3 (~200 °C). The phase transformation associated with boehmite occurs gradually within a broad temperature range. Furthermore, the NMR results show that the presence of $^{[5]}\text{Al}$ is accompanied by

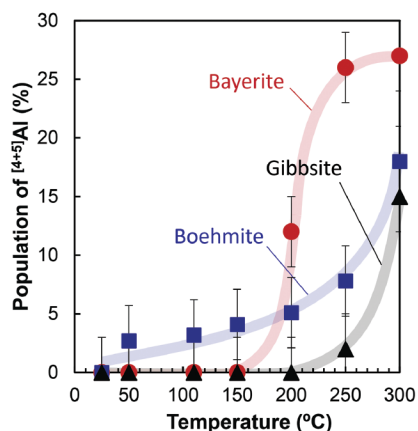


FIGURE 11. Variation in the $[4+3]\text{Al}$ fraction for boehmite (blue squares), bayerite (red circles), and gibbsite (black triangles) with varying temperatures. The smooth lines are to guide the eye only. (Color online.)

the phase transformation of boehmite $\rightarrow \gamma/\eta\text{-Al}_2\text{O}_3$, whereas the presence of $[5]\text{Al}$ is not evident in the gibbsite-derived $\gamma/\eta\text{-Al}_2\text{O}_3$. Note that several previous studies have suggested that the $[5]\text{Al}$ is located on the surface of $\gamma/\eta\text{-Al}_2\text{O}_3$ (e.g., Kwak et al. 2009; Lee et al. 2014 and references therein). Alternatively, the earlier NMR studies of amorphous Al_2O_3 -thin film indicated that the fractions of $[5]\text{Al}$ decrease with increasing thickness (Lee et al. 2009b, 2010; Lee and Ahn 2014). Based on these results, the fraction of $[5]\text{Al}$ in disordered/amorphous oxides is a proxy to the extent of structural disorder for bulk materials (Lee and Ahn 2014; Lee et al. 2016; Lee and Ryu 2018). The current results confirm that the extent of disorder of the boehmite-derived $\gamma/\eta\text{-Al}_2\text{O}_3$ is higher than that of the gibbsite-derived $\gamma/\eta\text{-Al}_2\text{O}_3$.

Therefore, the pronounced gradual phase transformation from boehmite to $\gamma/\eta\text{-Al}_2\text{O}_3$, which occurs from ~ 50 $^{\circ}\text{C}$, results from the moderate degree of structural disorder in boehmite, as also indicated from the broader X-ray diffraction peak. The difference in the extent of disorder in $\gamma/\eta\text{-Al}_2\text{O}_3$ associated with the types of precursor minerals results in the difference in the stability of metastable alumina.

Note that it is difficult to determine the phase transition temperature under 300 $^{\circ}\text{C}$, because the phase transformation in the low-temperature range can be kinetically broadened (e.g., Lee et al. 2020). Thus, further extensive study for kinetic nature of dehydration is necessary. While the previous studies have shown that the heating for more than ~ 2 h above 300 $^{\circ}\text{C}$ does not cause significant changes in the degree of phase transformation and/or dehydration (e.g., Xu and Smith 2012; Kim and Lee 2013a, 2013b; Lee and Ryu 2018 and references therein), the effect of annealing time on the dehydration in the low-temperature range remains to be explored. Furthermore, the stability fields of metastable aluminas are dependent on their physical properties (i.e., particle sizes, permeability, and surface area) (Sun et al. 2008; Kim and Lee 2013b; Karouia et al. 2016). Thus, the additional kinetic study of transformation with varying properties of aluminum (oxy)hydroxides remains to be considered. Nevertheless, the current results clearly demonstrate that the transformation path to metastable alumina depends on the type of precursor minerals.

IMPLICATIONS

The current ^{27}Al NMR results provide detailed information on the dehydration paths from three different aluminum (oxy)hydroxides (i.e., boehmite, bayerite, and gibbsite) to metastable alumina in the low-temperature range (≤ 300 $^{\circ}\text{C}$). By quantifying the populations of involving phases, the control of precursor minerals on the transformation paths have been systematically explored. The results demonstrate that the temperature ranges of phase transformation and the transformation paths (gradual vs. dramatic) depend on the extent of disorder of precursor minerals.

The precursor-dependent structural evolution in the low-temperature range would help to understand the geological processes involving metastable phases and their dehydration on the Earth's surface environments as the phase transformation involving metastable phases, such as $\gamma\text{-Al}_2\text{O}_3$, are common in the Earth's surface environments. For example, the recent rotary shear experiment of quartzite showed that the friction-induced melting at fault planes is partly controlled by the formation of metastable phase (such as metastable β -quartz), contributing to an overall fault-weakening (Lee et al. 2017). The melting temperature (i.e.,

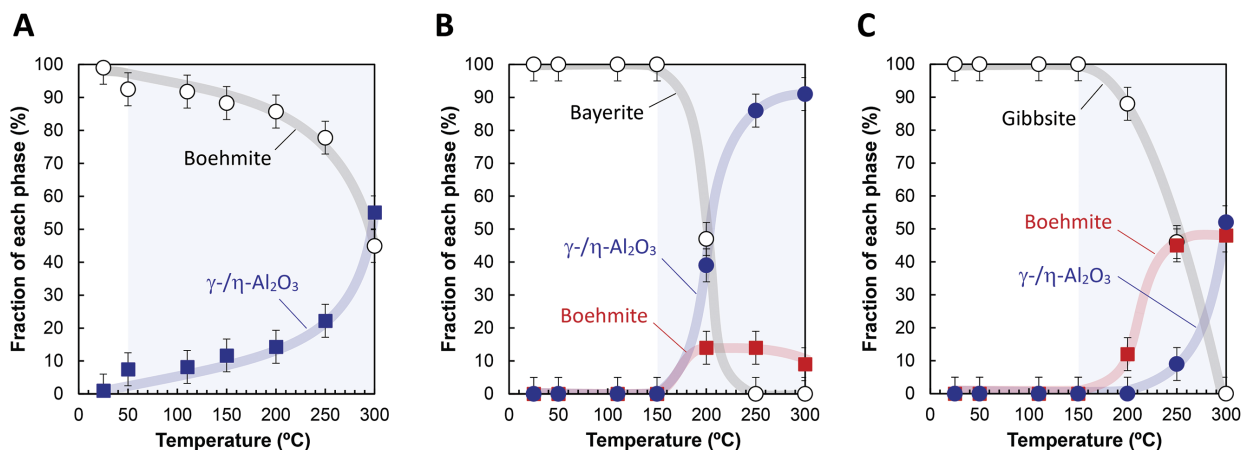


FIGURE 12. Variations in the populations of (a) boehmite and $\gamma/\eta\text{-Al}_2\text{O}_3$, (b) bayerite and $\gamma/\eta\text{-Al}_2\text{O}_3$ + boehmite, and (c) gibbsite, boehmite and $\gamma/\eta\text{-Al}_2\text{O}_3$ with varying annealing temperatures. The smooth lines are to guide the eye only. The shaded areas show the phase transformation temperature ranges from precursor minerals to metastable alumina. (Color online.)

threshold temperature) of metastable phase is much lower than the equilibrium transition temperature (Lee et al. 2017).

Furthermore, the reactivity of metastable oxides in contact with an aqueous solution depends on the short-range structures (e.g., electronic environment and network topology) (e.g., Phillips et al. 2000a, 2000b; Lee and Stebbins 2003; Lee and Weiss 2008; Li et al. 2010). Previous studies have shown that the ^{27}Al sites are known to control the overall catalytic ability of metastable alumina (e.g., Kwak et al. 2007, 2009; Lee et al. 2010). Because the formation of metastable Al_2O_3 with ^{27}Al may be prevalent at low-temperature condition ($\sim 50^\circ\text{C}$) as shown in the current study, the absorption of metal elements including rare-earth elements (REEs) on bauxite can be controlled by the presence of metastable alumina. It has been reported that the REEs are more enriched in boehmite-rich bauxite than in gibbsite-rich bauxite (e.g., Boni et al. 2013; Haniçlı 2013; Radusinović et al. 2017). While speculative, this difference in REE contents may stem from the presence of ^{27}Al (and thus its high catalytic activity) in the boehmite-derived metastable alumina at low temperature.

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