

## Online Materials

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

Hyo-Im Kim<sup>1</sup> and Sung Keun Lee<sup>1,2\*</sup>

<sup>1</sup>School of Earth and Environmental Sciences

Seoul National University

Seoul 08826, Korea

<sup>2</sup>Institute of Applied Physics

Seoul National University

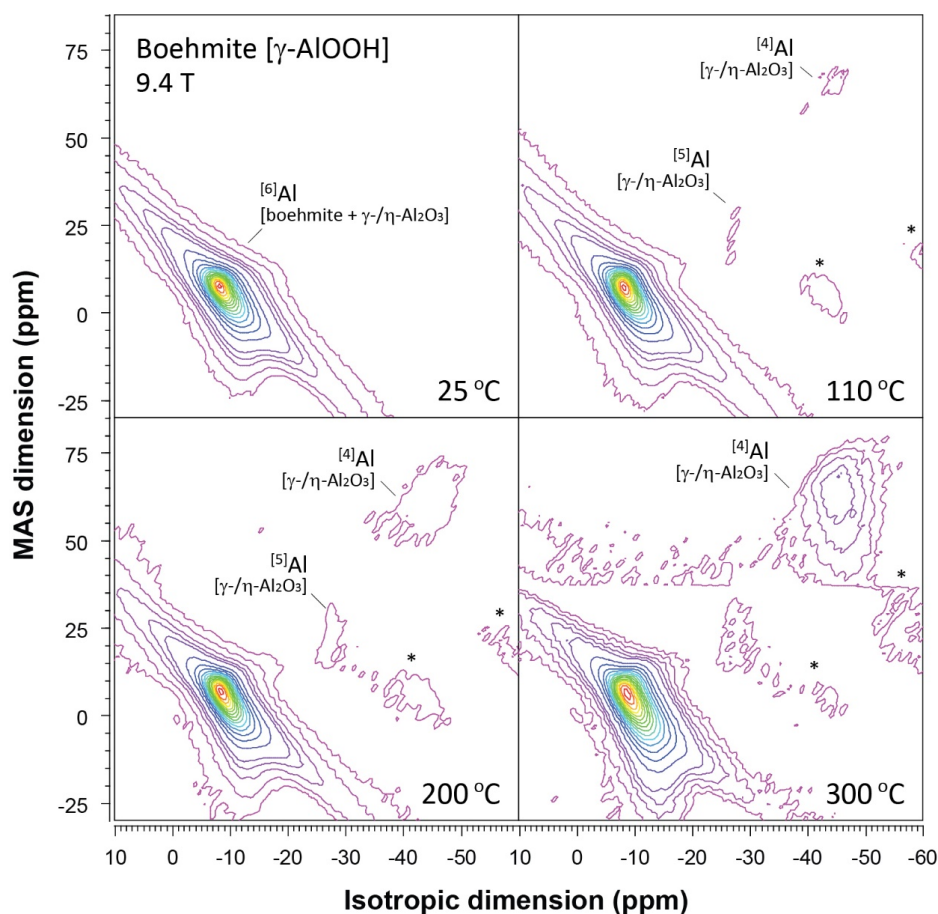
Seoul 08826, Korea

E-mail: sungklee@snu.ac.kr

Webpage: <http://hosting03.snu.ac.kr/~sungklee>

#### **SI-1. $^{27}\text{Al}$ 3QMAS NMR spectra for boehmite with varying annealing temperatures.**

Figure S1 presents the  $^{27}\text{Al}$  3QMAS NMR spectra for boehmite with varying annealing temperature without noise removal, showing that there is no observable noise with 1% contour line. To achieve current signal-to-noise ratio in the 2D spectra, ~16 hours of collection time were required for each spectra. Furthermore, better S/N ratio can be achieved by using a larger NMR rotor (i.e., 4 mm). This indicates that the minor fractions of  $^{4}\text{Al}$  and  $^{5}\text{Al}$  in the boehmite annealed at 110 °C and 200 °C do not stem from the noise. Note that there are small amount of noise at 1% contour lines for boehmite annealed at 300 °C. However, the  $^{4-6}\text{Al}$  peaks are clearly resolved from the noise. We also note that the signal from  $^{4,5,6}\text{Al}$  sites are not overlapped with the spinning sidebands, even at 15 kHz of spinning speed.



**Figure S1** |  $^{27}\text{Al}$  3QMAS NMR spectra (without noise removal) for boehmite with varying annealing temperature at 9.4 T and 15 kHz. The contour lines are drawn from 8% to 98% relative intensity with 6% increment and added lines at 1, 2.5, 4.5, and 6%.

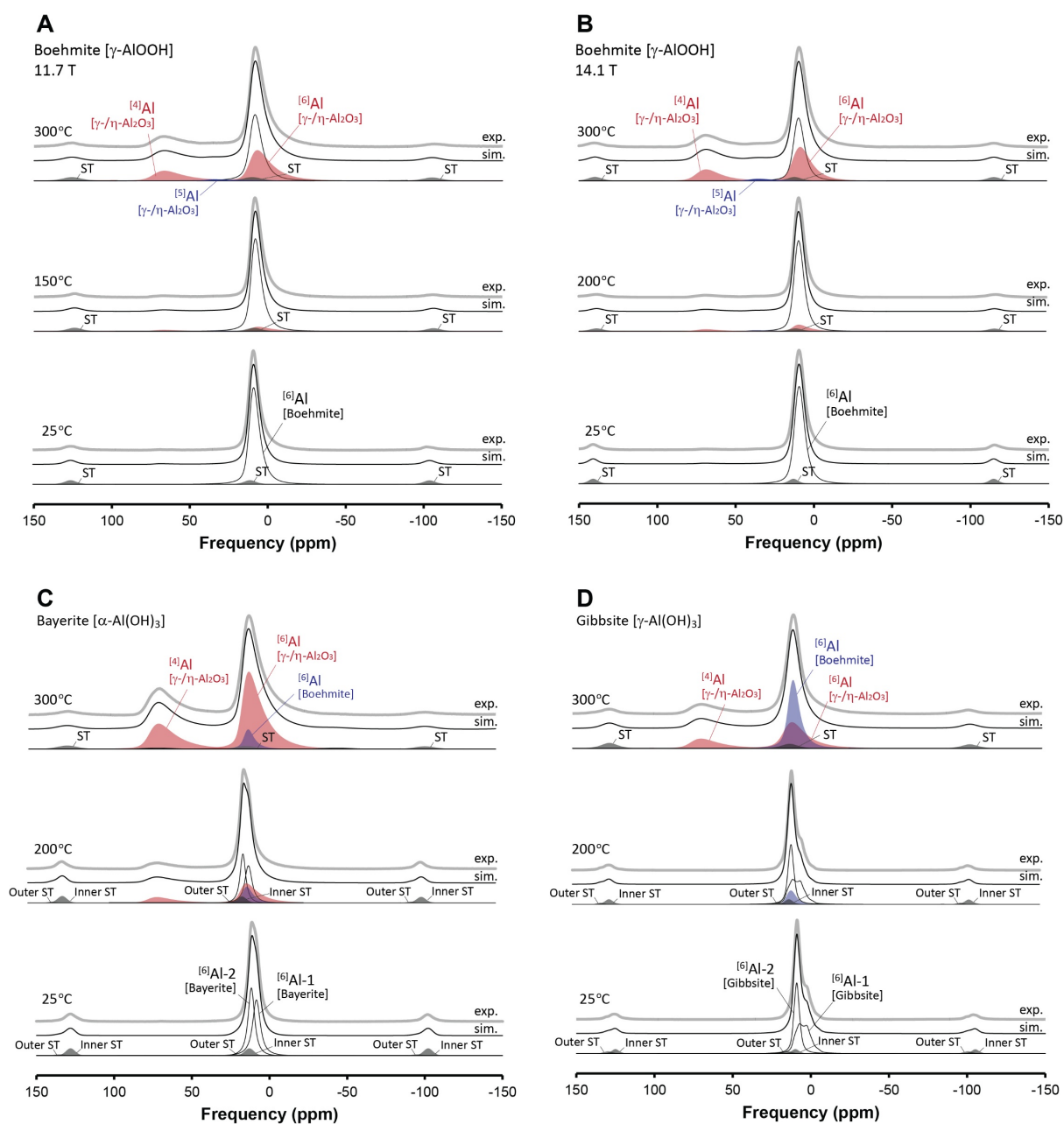
## SI-2. Simulation of $^{27}\text{Al}$ MAS NMR spectra using Dmfit.

The simulation of  $^{27}\text{Al}$  NMR spectra was performed with the Dmfit program (Massiot et al., 2002). 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., 2009; Park and Lee, 2019). The crystallographically inequivalent  $^{6}\text{Al}$  sites in the bayerite and gibbsite are difficult to distinguish in the 1D MAS NMR spectra. However, the extensive previous NMR studies using multi-quantum MAS techniques and quantum chemical calculations have reported the NMR parameters [i.e., isotropic chemical shift ( $\delta_{\text{iso}}$ ), quadrupolar constant ( $C_q$ ), and asymmetry parameter ( $\eta$ )] of each site in bayerite and gibbsite (Damodaran et al., 2002; Vyalikh et al., 2010; Chandran et al., 2019). As shown in Table 2, the NMR parameters of bayerite and gibbsite are well-documented. The spectra

for boehmite and metastable alumina were fitted using a Gaussian isotropic model distribution (GIM, case of  $d = 5$  of the more general Czjzek 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., 2009; Kim and Lee, 2013 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). In the current study, the NMR parameters and relative fractions were obtained by manual adjustment of input parameters (such as  $\delta_{\text{iso}}$ ,  $C_q$ ,  $\Delta\delta_{\text{iso}}$ , and broadening factors). The  $\Delta\delta_{\text{iso}}$  is the full-width at half maximum of the distribution of the isotropic chemical shift in the Czjzek model, which is used for simulation of the  $^{41}\text{Al}$  and  $^{61}\text{Al}$  peaks for  $\gamma$ -/ $\eta$ - $\text{Al}_2\text{O}_3$ . The Gaussian or Lorentzian broadening factor ( $\sim 300$  to  $2000$  Hz) is applied to simulate Al sites for each phase. Note that the possible uncertainties stemming from the deviation between experimental and simulated spectra ( $\sim 1.5\%$ ) and the contribution from the adjusted input parameters ( $\sim 1.5\%$ ) were included in the errors in the estimation of Al fractions and phase fractions.

### SI-3. Simulation of $^{27}\text{Al}$ MAS NMR spectra with central transition and satellite spinning sidebands

The spinning sidebands due to satellite transition often overlap with the central bands. Thus, the contribution of satellite transition to NMR intensity needs to be considered to get robust fraction of Al site in each phase (e.g., Kraus et al., 1998; Lee and Stebbins, 2003 and references therein). As shown in Figure S2, the current  $^{27}\text{Al}$  MAS NMR spectra for three different types of aluminum (oxy)hydroxides with varying temperatures were simulated by considering the satellite transition spinning sideband (using Dmfit) (Massiot et al., 2002). Note that the simulations of spinning sideband for highly-ordered crystalline phases (i.e., gibbsite and bayerite) were performed with both the inner ( $\pm 1/2 \leftrightarrow \pm 3/2$ ) and outer ( $\pm 5/2 \leftrightarrow \pm 3/2$ ) satellite transitions. The difference in the estimated fractions of each phase at given temperature between simulation results with considering and without considering contribution of satellite transitions is  $\sim 1$ - $2\%$ : for example, the obtained fractions of  $\gamma$ -/ $\eta$ - $\text{Al}_2\text{O}_3$  for boehmite annealed at  $300^\circ\text{C}$  are  $\sim 38\%$  (without consideration) and  $\sim 37\%$  (with consideration), respectively. Nevertheless, the possible uncertainties from the spinning sidebands on the NMR intensities ( $\sim 1.5\%$ ) were included in the errors in the estimation of Al fractions and phase fractions.



**Figure S2** | Simulation of  $^{27}\text{Al}$  MAS NMR spectra for three different types of aluminum (oxy)hydroxides [(A) boehmite at 11.7 T, (B) boehmite at 14.1 T, (C) bayerite, and (D) gibbsite] with varying temperatures (as labeled) with considering the contribution of satellite transitions.

## References

- Chandran, C.V., Kirschhock, C.E.A., Radhakrishnan, S., Taulelle, F., Martens, J.A., and Breynaert, E. (2019) Alumina: discriminative analysis using 3D correlation of solid-state NMR parameters. *Chemical Society Reviews*, 48(1), 134-156.
- Damodaran, K., Rajamohanan, P.R., Chakrabarty, D., Racherla, U.S., Manohar, V., Fernandez, C., Amoureux, J.P., and Ganapathy, S. (2002) Triple-quantum magic angle spinning Al-27 NMR of aluminum hydroxides. *Journal of the American Chemical Society*, 124(13), 3200-3201.
- Kim, H.N., and Lee, S.K. (2013) Effect of particle size on phase transitions in metastable alumina nanoparticles: A view from high-resolution solid-state Al-27 NMR study. *American Mineralogist*, 98(7), 1198-1210.
- Kraus, H., Muller, M., Prins, R., and Kentgens, A.P.M. (1998) Comments on the Al-27 NMR visibility of aluminas. *Journal of Physical Chemistry B*, 102(20), 3862-3865.
- Le Caer, G., and Brand, R.A. (1998) General models for the distributions of electric field gradients in disordered solids. *Journal of Physics-Condensed Matter*, 10(47), 10715-10774.
- Lee, S.K., Deschamps, M., Hiet, J., Massiot, D., and Park, S.Y. (2009) Connectivity and proximity between quadrupolar nuclides in oxide glasses: insights from through-bond and through-space correlations in solid-state NMR. *Journal of Physical Chemistry B*, 113(15), 5162-7.
- Lee, S.K., and Stebbins, J.F. (2003) O atom sites in natural kaolinite and muscovite: O-17 MAS and 3QMAS NMR study. *American Mineralogist*, 88(4), 493-500.
- Massiot, D., Fayon, F., Capron, M., King, I., Le Calve, S., Alonso, B., Durand, J.O., Bujoli, B., Gan, Z.H., and Hoatson, G. (2002) Modelling one- and two-dimensional solid-state NMR spectra. *Magnetic Resonance in Chemistry*, 40(1), 70-76.
- Neuville, D.R., Cormier, L., and Massiot, D. (2004) Al environment in tectosilicate and peraluminous glasses: A Al-27 MQ-MAS NMR, Raman, and XANES investigation. *Geochimica Et Cosmochimica Acta*, 68(24), 5071-5079.
- Park, S.Y., and Lee, S.K. (2019) Effect of composition on isotropic chemical shift of Na silicate and aluminosilicate glasses using solid state NMR. *Journal of the Mineralogical Society of Korea*, 32(1), 41-49.
- Vyalikh, A., Zesewitz, K., and Scheler, U. (2010) Hydrogen bonds and local symmetry in the crystal structure of gibbsite. *Magnetic Resonance in Chemistry*, 48(11), 877-881.