Electronic Supplementary Information

[A]

We conducted preliminary TG measurements in order to determine appropriate hydration conditions where the supply rate of water vapor does not limit the hydration reaction rate of \( \beta - \text{La}_2(\text{SO}_4)_3 \). Figure S1 shows TG curves on the hydration reaction under 200 and 100 mL min\(^{-1}\) of humidified argon gas flowing. There was no difference in the hydration reaction rate between these two TG curves. This suggested that 200 mL min\(^{-1}\) of argon gas flowing was enough for preventing the hydration reaction rate from being limited by the flow rate. Figure S2 shows TG curves on the hydration reaction obtained by using three different weight of \( \beta - \text{La}_2(\text{SO}_4)_3 \) samples: 7.7, 14 and 34 mg. The hydration reaction rate of 34 mg of \( \beta - \text{La}_2(\text{SO}_4)_3 \) sample was significantly slower than those of the other two cases. This suggests that the hydration reaction of 34 mg of sample was influenced by water diffusion in particle interstices, while either 7.7 and 14 mg of sample gives TG curves without influence of rate of water vapor supply. For obtaining precise TG curves with small signal/noise ratio, 14 mg was better. Therefore, we conducted TG measurements under 200 mL min\(^{-1}\) of argon gas flowing and using about 14 mg of \( \beta - \text{La}_2(\text{SO}_4)_3 \) sample.
Figures S1. TG curves on the hydration reaction under 200 (black line) and 100 (red dashed line) mL min\(^{-1}\) of argon gas flowing. Temperatures during measurement fluctuated ± 2.5 °C. About 30 mg of \(\beta\)-La\(_2\)(SO\(_4\))\(_3\) was used for each measurement.

Figures S2. TG curves on the hydration reaction of three different weight of \(\beta\)-La\(_2\)(SO\(_4\))\(_3\) samples: 7.7 (blue dotted line), 14 (black line) and 34 mg (red dashed line). Temperatures during measurement fluctuated ± 2.5 °C. Wet and dry argon gas was flowed at a rate of 200 mL min\(^{-1}\).
The phases in this study were identified by XRD measurements. Figure S3 and S4 are examples of the XRD patterns. Figure S3 shows XRD patterns of the sample in each dehydration process used for the EPMA observations (subsection 3.1). The figure indicates that phases in figure 2 (a), (b), and (c) were $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, amorphous $\text{La}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, and $\beta$-$\text{La}_2(\text{SO}_4)_3$ respectively. Figure S4 shows XRD patterns of the sample after three times of nitrogen gas adsorption measurements in sequence with different pretreatment (subsection 3.2). The figure indicates that the phases of sample corresponding with three isotherms in Figure 3 were $\text{La}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$, amorphous $\text{La}_2(\text{SO}_4)_3 \cdot n\text{H}_2\text{O}$, and $\beta$-$\text{La}_2(\text{SO}_4)_3$. 

[B]
**Figure S3.** XRD patterns of the lanthanum sulfate sample in each dehydration process used for EPMA observations. (a) La$_2$(SO$_4$)$_3$·9H$_2$O as received. X-ray was irradiated to the sample on carbon tape. (b) After heating of La$_2$(SO$_4$)$_3$·9H$_2$O at 170 °C for 60 minutes with carbon tape and cooled to room temperature. (c) After heating the sample used in (b) at 270 °C for 30 minutes with carbon tape and cooled to room temperature.

* The reference pattern of β-La$_2$(SO$_4$)$_3$ shown in (c) was calculated using VESTA $^1$ based on crystal structure of Nd$_2$(SO$_4$)$_3$ reported by Sirotinkin $^2$ with following modification.

- Nd atoms of Nd$_2$(SO$_4$)$_3$ were replaced with La atoms
- Lattice parameters were adjusted to match measured angles of XRD peak by least square method.

These values are $a = 22.058$ Å, $b = 7.0817$ Å, $c = 6.8333$ Å, $\alpha = \beta = 90^\circ$, $\gamma = 109.43^\circ$
Figure S4. XRD patterns of the lanthanum sulfate samples after three times of nitrogen gas adsorption measurements in sequence with different pretreatments. These pretreatment conditions are (a) just vacuuming at room temperature for about 18 hours, (b) vacuum-heating at 100 °C for 3 hours, and (c) vacuum-heating at 300 °C for 3 hours.

* The reference pattern of β-La$_2$(SO$_4$)$_3$ shown in (c) was calculated by the same method explained in Figure S3 (c). Applied lattice parameters are shown below.

\[
a = 21.972 \text{ Å}, \quad b = 7.0676 \text{ Å}, \quad c = 6.7818 \text{ Å}, \quad \alpha = \beta = 90^\circ, \quad \gamma = 109.27^\circ
\]


We estimated the density of amorphous La$_2$(SO$_4$)$_3$·$n$H$_2$O from reported densities of other lanthanum sulfate hydrates: La$_2$(SO$_4$)$_3$·9H$_2$O$^1$, La$_2$(SO$_4$)$_3$·4H$_2$O$^2$, and β-La$_2$(SO$_4$)$_3$ $^3$. Figure S5 shows relationships between hydration number and density of lanthanum sulfate hydrates. The densities of hydrates are linearly dependent on hydration number $n$. Our previous TG measurements$^3$ revealed that the hydration number of amorphous La$_2$(SO$_4$)$_3$·$n$H$_2$O range from 1 to 3. Figure S5 suggests that the density of amorphous La$_2$(SO$_4$)$_3$·$n$H$_2$O is estimated to be from 3.47 to 3.67 g cm$^{-3}$. We conducted BET-method analysis based on the estimated density of amorphous La$_2$(SO$_4$)$_3$·$n$H$_2$O. The average particle size $d$ was calculated to be from 8.4 to 8.7 μm.

Figure S5. Relationships between hydration number and density of lanthanum sulfate hydrates.

[2] Shi B., “Preparation and crystal structure of Ln$_2$(SO$_4$)$_3$(H$_2$O)$_4$ (Ln= La, compound I; Nd, compound II)”, *J. Struct. Chem. (China)* 1987, 6, 70.
We estimated $\tau_{90\%_{\text{exp}}}$ by fitting of TG curves to avoid possible error in defining the final weight.

Solution of one-dimensional diffusion equation (2) was expediently used for the fittings. Figure S6 show TG curves and fitting curves. Here, average values of hydration number in 1200 seconds before the start of wet gas flowing were used as $w^{(0)}$ in equation (2). End of fitting section of TG curves are time where hydration reaction mostly completed: 6000 seconds for green and red TG curves, and 3000 seconds for blue TG curves. Although equation (2) is too simple to represent actual hydration reaction, it gives good fits to experimental results with errors less than several minutes.

**Figure S6.** TG curves and their fitted curves (dashed lines) of small- and large-particle $\beta$-$\text{La}_2(\text{SO}_4)_3$ at constant temperatures. The temperature during measurements fluctuated ± 1 °C. TG curves of each sample were collected at three different temperatures: 36.1 and 37.4 °C (green line), 55.3 and 56.1 °C (red line), and 72.9 and 73.8 °C (blue line).