

Electronic supplementary information (ESI)

Impact of cationic lanthanum species on zeolite Y: an infrared, excess infrared and Raman spectroscopic study

Nan-Nan Wang,^{*a,b} Yong Wang,^a Hai-Feng Cheng,^b Zhi Tao,^a Jun Wang^b and Wei-Zu Wu^b

^a Beijing Institute of Information Technology, Beijing 100094, People's Republic of China

^b Key Laboratory of Science and Technology on Advanced Ceramic Fibers and Composites, College of Aerospace Science and Engineering, National University of Defense Technology, Changsha, Hunan 410073, People's Republic of China

Corresponding Author

* Tel (+86) 731 84575158; Fax (+86) 731 84576578; E-mail: nnnwang@vip.163.com.

A. Deduction of excess infrared spectroscopy for solid system

The theory of excess infrared spectroscopy has been described in detail elsewhere.^{S1} Briefly, an excess infrared spectrum is defined as the difference between the spectrum of a real solution and that of the respective ideal solution under identical conditions. The working equation used to calculate the excess infrared spectrum of two components in liquid state is

$$\varepsilon^E = \frac{A}{d(C_1 + C_2)} - (x_1\varepsilon_1^* + x_2\varepsilon_2^*) \quad (\text{S1})$$

where A is the absorbance of the mixture, d is the light path length, C_1 and C_2 are molarities of the two components, x_1 and x_2 are the mole fractions of components 1 and 2, respectively, and ε_1^* and ε_2^* are the molar absorption coefficients of the two components in their pure states, respectively. ε_1^* and ε_2^* can be calculated following the Beer–Lambert Law:

$$A = \varepsilon dC \quad (\text{S2})$$

By considering $\varepsilon_1^* = A_1^*/d_1^*C_1^*$, $\varepsilon_2^* = A_2^*/d_2^*C_2^*$, $x_1 = C_1/(C_1+C_2)$, and $x_2 = C_2/(C_1+C_2)$, the working equation used to calculate the excess infrared spectrum can be expressed as

$$\varepsilon^E = \frac{A}{d(C_1 + C_2)} - \left(\frac{C_1}{C_1 + C_2} \frac{A_1^*}{d_1^*C_1^*} + \frac{C_2}{C_1 + C_2} \frac{A_2^*}{d_2^*C_2^*} \right) \quad (\text{S3})$$

Following the definition of molarity in solutions, we assume that the molarity of a solid sample diluted by KBr can be calculated using the following expression:

$$C = \frac{m}{MV} \quad (\text{S4})$$

where m is the mass of the investigated solid component, M is the formula weight of the component, V is the total volume of the KBr pellet containing the solid sample and KBr.

An internal standard (IS) was used to determine the light path length of each sample. The standard absorption band of the IS should not overlap with the bands of the samples considered. Moreover, its molar absorption coefficient should also not be affected by the presence of the samples. According to the Beer–Lambert Law, the light path length can be calculated by the integral area of the standard band:

$$d = \frac{A_{\text{IS}}}{\varepsilon_{\text{IS}} C_{\text{IS}}} \quad (\text{S5})$$

where C_{IS} can be calculated using eqn (S4).

Combining eqn (S3~S5), i.e., replacing d and C in eqn (S3) with the measurable quantities of the solid system, such as m , V , and A , we obtain the following expression:

$$\varepsilon^{\text{E}} = \varepsilon_{\text{IS}} \frac{1}{M_{\text{IS}} \left(\frac{m_1}{M_1} + \frac{m_2}{M_2} \right)} \left[\frac{m_{\text{IS}}}{A_{\text{IS}}} A - \left(\frac{m_1}{m_1^*} \frac{m_{\text{IS},1}^*}{A_{\text{IS},1}^*} A_1^* + \frac{m_2}{m_2^*} \frac{m_{\text{IS},2}^*}{A_{\text{IS},2}^*} A_2^* \right) \right] \quad (\text{S6})$$

where ε_{IS} is a constant for a certain IS. Thus, the total volume of each sample, which is difficult to measure accurately, has been eliminated. Eqn (S6) is the working equation used to calculate the excess infrared spectrum of a solid system.

B. Experimental details

B1. Infrared spectroscopy

Weights of samples were measured by an analytical balance with an accuracy of ± 0.1 mg. Abundant samples were prepared for 3 parallel experiments and reducing the uncertain in weighing. A mixture of ~ 5 g dry KBr (m_{KBr}) and 3~3.5 mg KSCN (m_{KSCN}) was fully mixed through grinding. Subsequently, 1~1.5 mg LaNaY (m_{LaNaY}) was added to ~ 1 g KBr/KSCN mixture ($m_{\text{KBr/KSCN}}$), obtaining uniform mixture through grinding. ~ 0.15 g LaNaY/KBr/KSCN was taken to prepare each KBr pellet and the mass of the pellet ($m_{\text{LaNaY/KBr/KSCN}}$) was weighed immediately after infrared spectroscopic measurement. The sample amounts above were decided experimentally by getting moderate absorption

bands of the SCN^- stretching and the asymmetric TO_4 stretching, with the maximum absorbance between 0.3~0.6.

In LaNaY system, component 2 is the whole encapsulated species, including lanthanum and sodium species, indicating M_2 in eqn (S6) is a variable as a function of lanthanum content. However, considering that component 2 does not have absorptions in the region of asymmetric TO_4 stretches, namely, A_2^* is equal to 0, the working equation for calculating the excess infrared spectrum of LaNaY system is

$$\varepsilon^E = \varepsilon_{\text{IS}} \frac{1}{M_{\text{IS}} \left(\frac{m_1}{M_1} + \frac{m_2}{M_2} \right)} \left[\frac{m_{\text{IS}}}{A_{\text{IS}}} A - \frac{m_1}{m_1^*} \frac{m_{\text{IS},1}^*}{A_{\text{IS},1}^*} A_1^* \right] \quad (\text{S7})$$

where m_2/M_2 represents the amount of substance of component 2, equal to the summation of mole numbers of lanthanum species and sodium species. Therefore, m_2/M_2 , substituting M_2 , is used in this work.

In summary, the quantities in eqn (S7) are determined as follow

ε_{IS} : constant, retained in the results of ε^E .

M_{IS} : 97.2, the formula weight of KSCN.

m_1 : $m_{\text{LaNaY}} m_{\text{LaNaY/KBr/KSCN}} w_{\text{framework}} / (m_{\text{LaNaY}} + m_{\text{KBr/KSCN}})$, $w_{\text{framework}}$ is the mass fraction of $(\text{Si}_{0.717}\text{Al}_{0.283}\text{O}_2)$, calculating by $(2.1w_{\text{Si}} + 2.2w_{\text{Al}})$ in each sample. w_{Si} and w_{Al} were determined by ICP-AES.

M_1 : 59.3, the formula weight of the average chemical compositions of faujasite framework $(\text{Si}_{0.717}\text{Al}_{0.283}\text{O}_2)$ in zeolite Y with an $n_{\text{Si}}/n_{\text{Al}}$ ratio of 2.53.

m_2/M_2 : $m_{\text{LaNaY}} m_{\text{LaNaY/KBr/KSCN}} w_{\text{La}} / [138.9(m_{\text{LaNaY}} + m_{\text{KBr/KSCN}})] + m_{\text{LaNaY}} m_{\text{LaNaY/KBr/KSCN}} w_{\text{Na}} / [23.0(m_{\text{LaNaY}} + m_{\text{KBr/KSCN}})]$, 138.9 and 23.0 represent the relative atomic mass of lanthanum and sodium element respectively. w_{La} and w_{Na} were determined by ICP-AES.

m_{IS} : $m_{\text{KSCN}} [m_{\text{KBr/KSCN}} / (m_{\text{KBr}} + m_{\text{KSCN}})] [m_{\text{LaNaY/KBr/KSCN}} / (m_{\text{LaNaY}} + m_{\text{KBr/KSCN}})]$.

A_{IS} : integral area of SCN^- stretching absorption of the sample considered.

m_1^* , $m_{\text{IS},1}^*$, $A_{\text{IS},1}^*$: quantities of component 1 under ideal state, calculated as discussed above. Ideal state of component 1 is LaNaY-reh-0, LaNaY-hyd-0, and LaNaY-reh-0 in the three series of excess infrared spectra (LaNaY-hyd-0 relative to LaNaY-reh-0, LaNaY-hyd system, and LaNaY-reh systems) in this study respectively.

A : absorbance in the spectrum of the sample considered.

A_1^* : absorbance in the spectrum of component 1 under ideal state.

B2. Raman spectroscopy

Take NaY and LaNaY-reh-6.6% as examples, the samples show legible Raman bands under an excitation source at 532 nm, even without pretreatment (Fig. S1). However, the fluorescence interference of the background decreased as a function of irradiation time. Since fluorescence interference is extremely severe for most microporous materials due to the fluorescence impurity such as the templates,^{S2} the fluorescing species in this work is attributed to trace organic impurity. We also found that the crude Raman spectra of the samples reached a constant value after irradiation under the laser at 532 nm for approximate 400~600 s (Fig. S1), while the bands of zeolite framework were not impacted by the irradiation. Therefore, 10 min's irradiation has been selected for all the samples to eliminate the fluorescence. Photo-dissociating, and/or inter-system crossing of the organic impurity play important roles in the photo-bleaching process.^{S3} As shown in Fig. S1, no band of the photo-products appears.

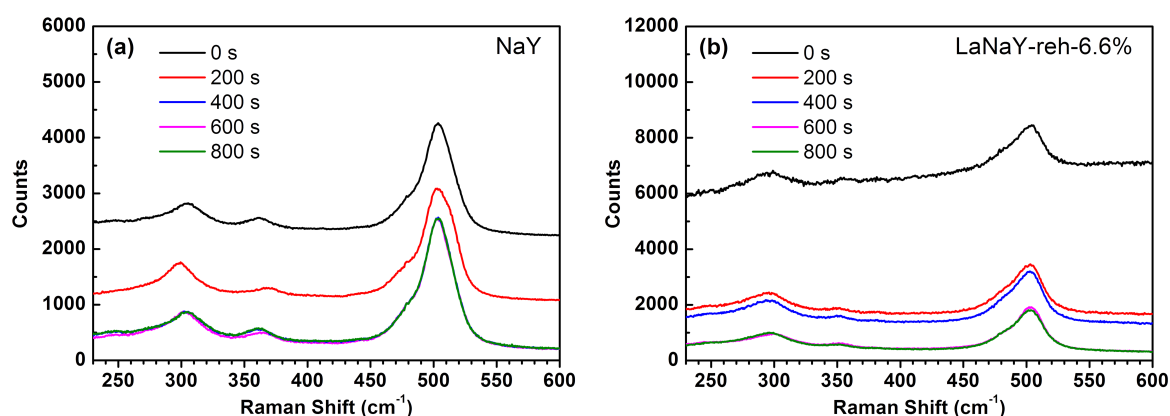


Fig. S1 Crude Raman spectra of (a) NaY and (b) LaNaY-reh-6.6% as a function of irradiation time.

C. Deconvolution procedure

Deconvolution of the excess infrared, Raman, and NMR spectra was carried out using the curve fitting routine provided by PeakFit 4.0 software (AISN Software Inc.). The peak type was Gaussian+Lorentz for all the deconvolution treatments. Taking the excess infrared spectrum of LaNaY-reh-12.5% as an example, the deconvolution procedure is illustrated in Fig. S2. The similarity of original and generated curves is represented by correlation coefficient (R^2). The value of R^2 is always between 0 and 1, with 0 meaning that the two curves are completely uncorrelated, 1 meaning they are identical. In the

optimization process by PeakFit 4.0 software, R^2 is related to the number and positions of the component bands assigned manually (Fig. S2b). In this work, the number and approximate positions of the component bands were determined by analyzing the asymmetry of the band (excess infrared and Raman spectra) or according to the literatures (^{27}Al and ^{29}Si MAS NMR spectra), while the final position and the intensity of each component band were optimized by the software (Fig. S2c). A value of R^2 larger than 0.99 was taken as a criterion to finish the deconvolution.

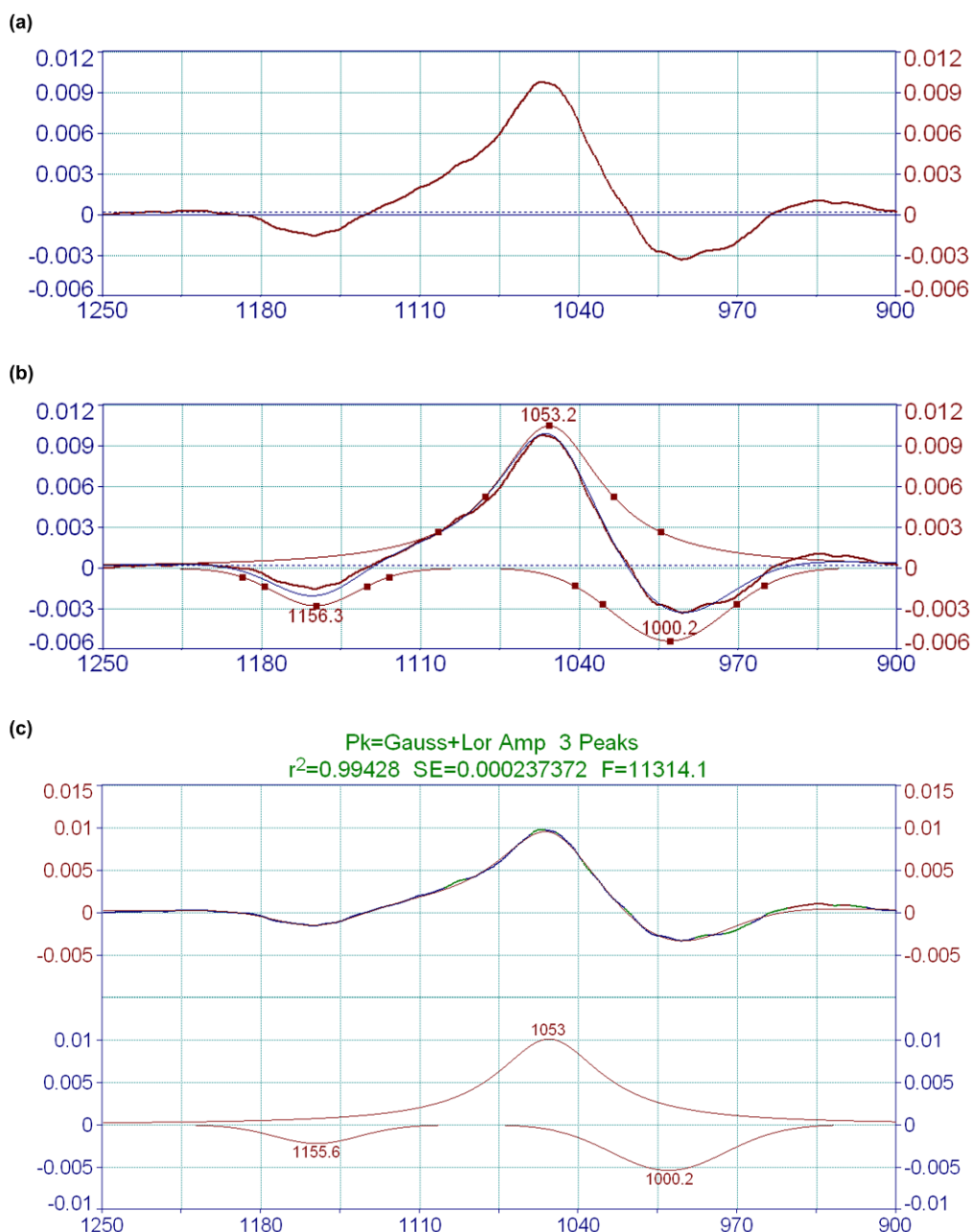


Fig. S2 Active windows in PeakFit 4.0 software in the deconvolution process of excess infrared spectrum of LaNaY-reh-12.5%. (a) Opening the spectroscopic data. (b) Assigning the number and approximate positions of the component bands manually. (c) Deconvolution result optimized by the software with a $R^2=0.99428$.

D. Deconvolution results of excess infrared spectra of LaNaY-reh system

The deconvolution results of excess infrared spectra in the asymmetric TO_4 stretching vibrational region of LaNaY-reh system over the full concentration range are listed in Fig. S3. The peak positions and integral areas of the deconvolution results are plotted in Fig. S4.

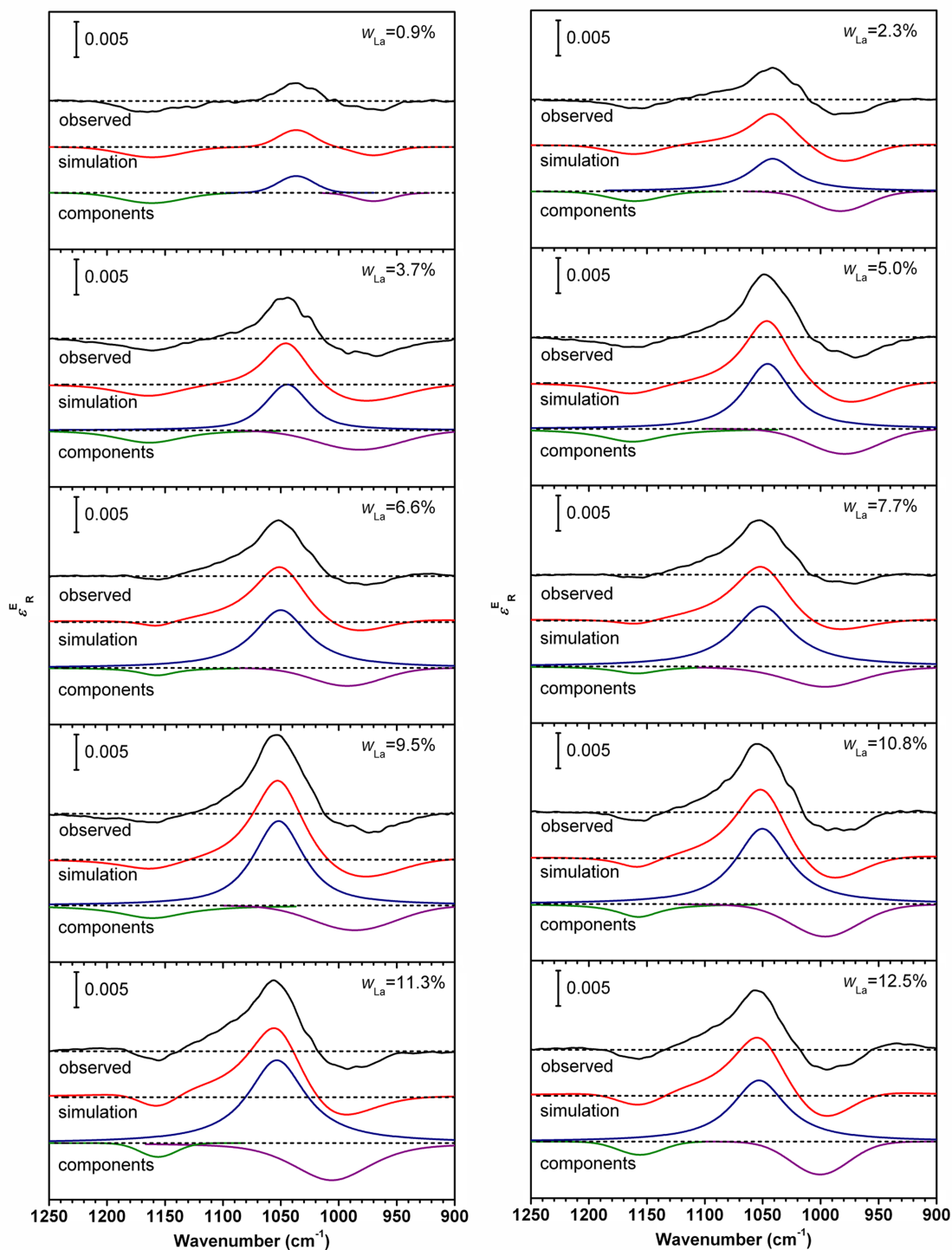


Fig. S3 Deconvolution results of excess infrared spectra of LaNaY-reh system.

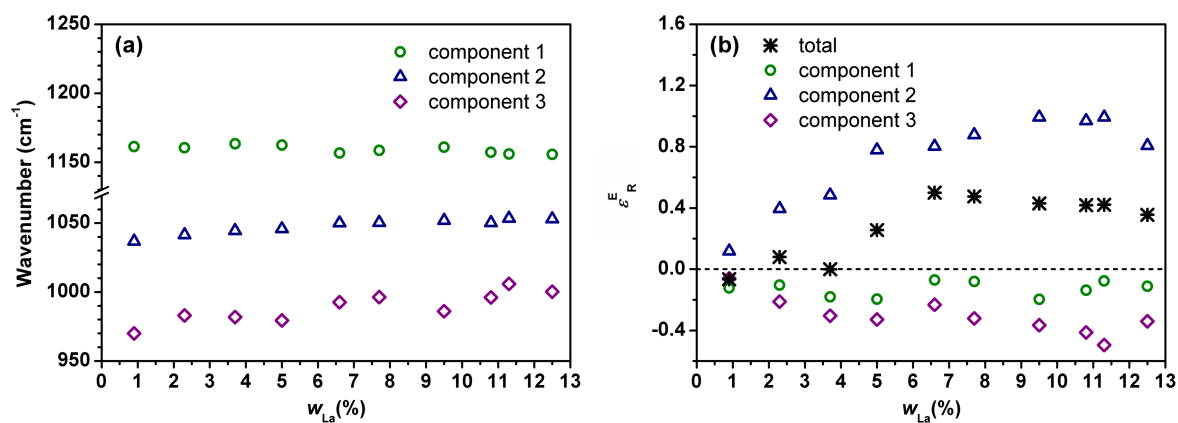


Fig. S4 (a) Peak positions and (b) integral intensities of the component bands in Fig. S3.

E. Deconvolution results of T–O–T bending of 4-membered rings in Raman spectra

The deconvolution results of T–O–T bending of 4-membered rings in the Raman spectra of LaNaY-hyd and LaNaY-reh systems over the full concentration range are listed in Fig. S5 and Fig. S6, respectively.

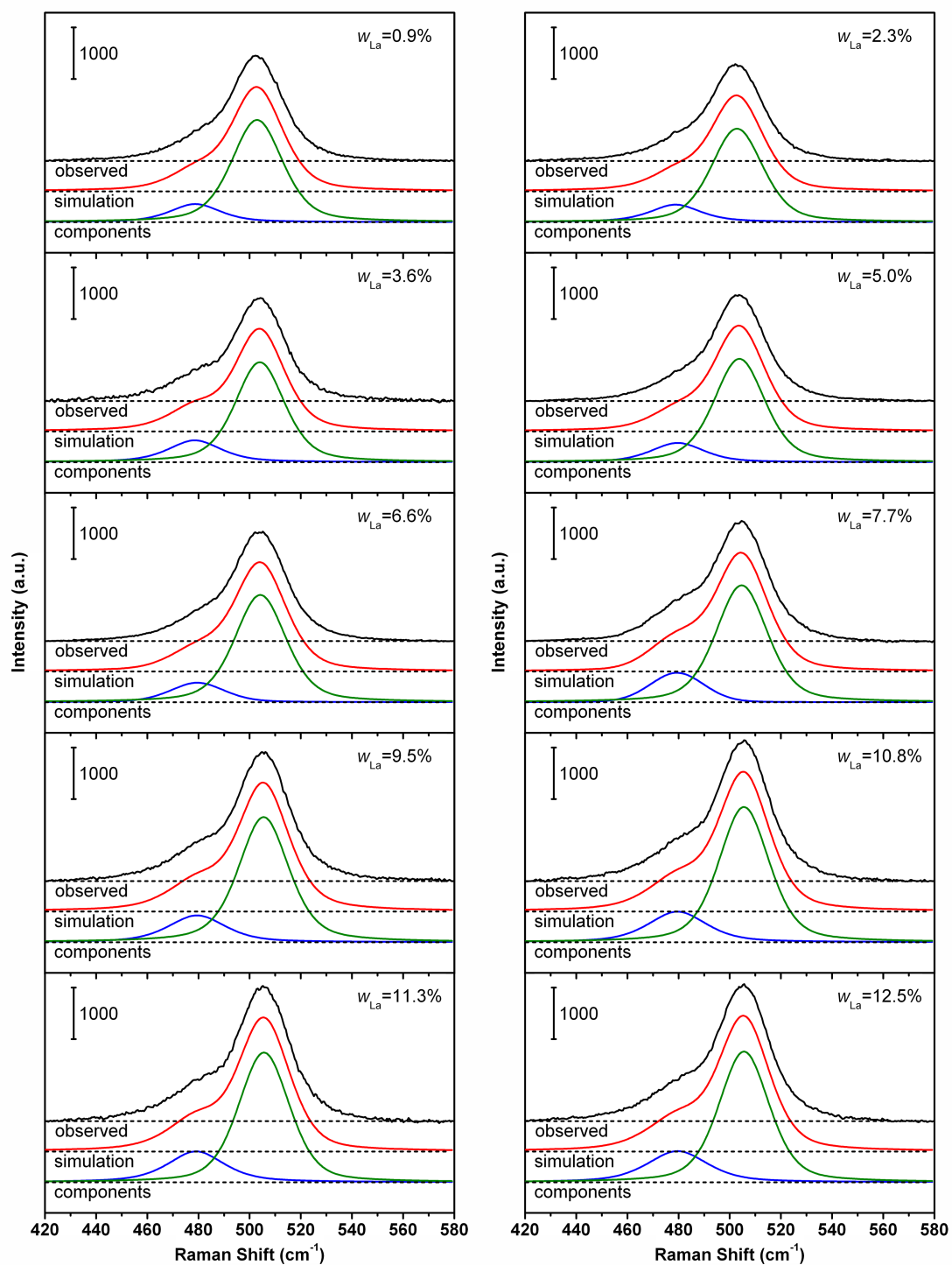


Fig. S5 Deconvolution results of T-O-T bending bands of 4-membered rings in the Raman spectra of LaNaY-hyd system.

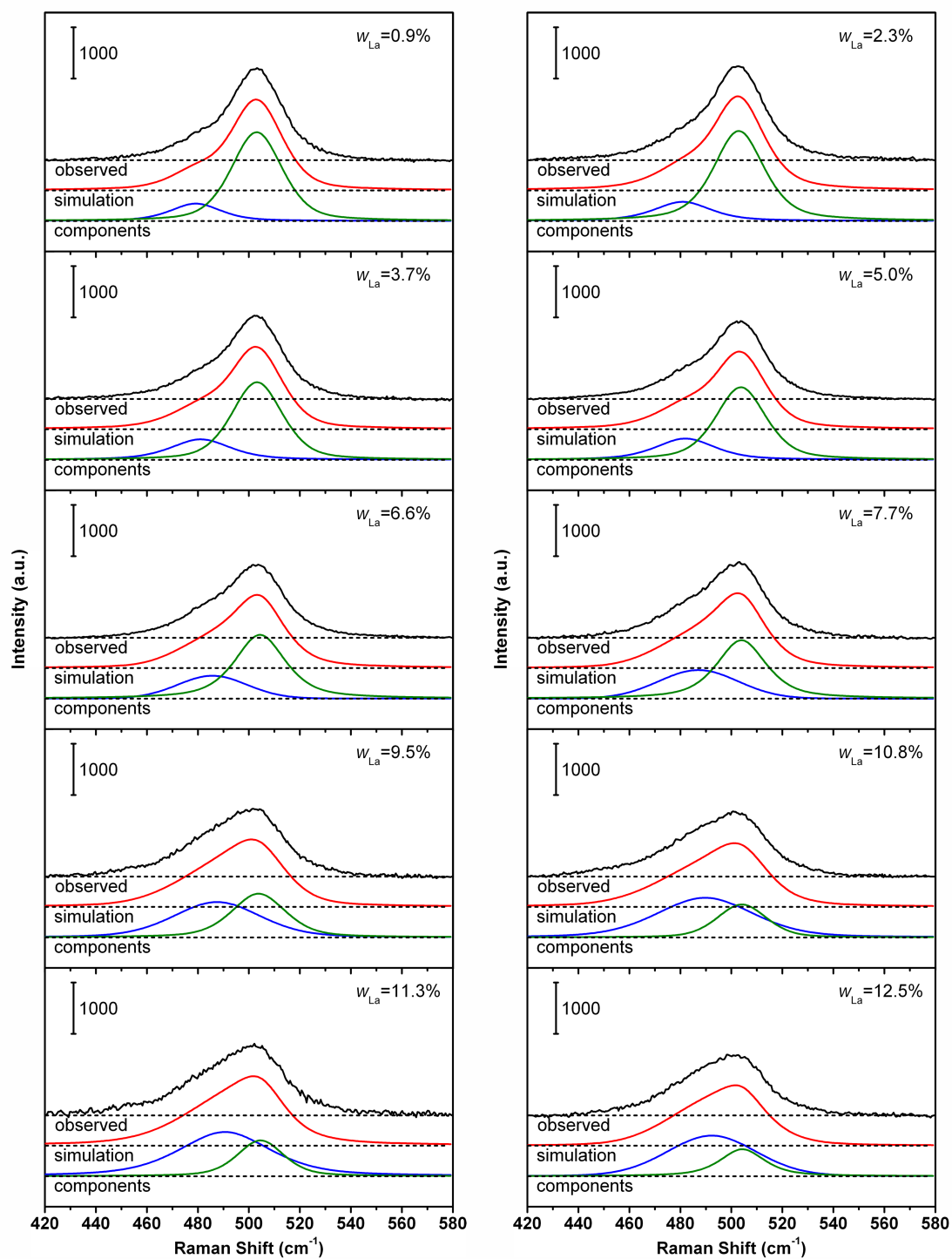


Fig. S6 Deconvolution results of T–O–T bending bands of 4-membered rings in the Raman spectra of LaNaY-reh system.

F. Deconvolution results of ^{27}Al and ^{29}Si MAS NMR spectra

The deconvolution results of ^{27}Al and ^{29}Si MAS NMR spectra are listed in Fig. S7 and Fig. S8, respectively.

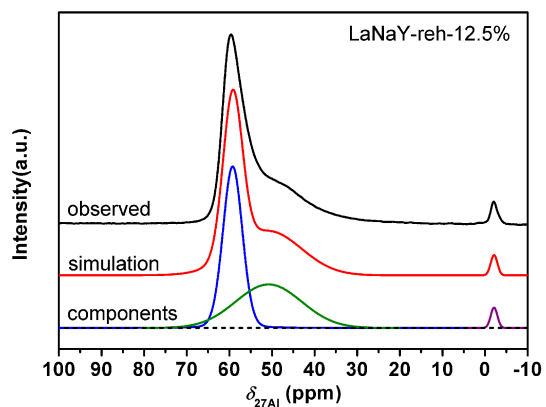


Fig. S7 Deconvolution result of ^{27}Al MAS NMR spectrum of LaNaY-reh-12.5%.

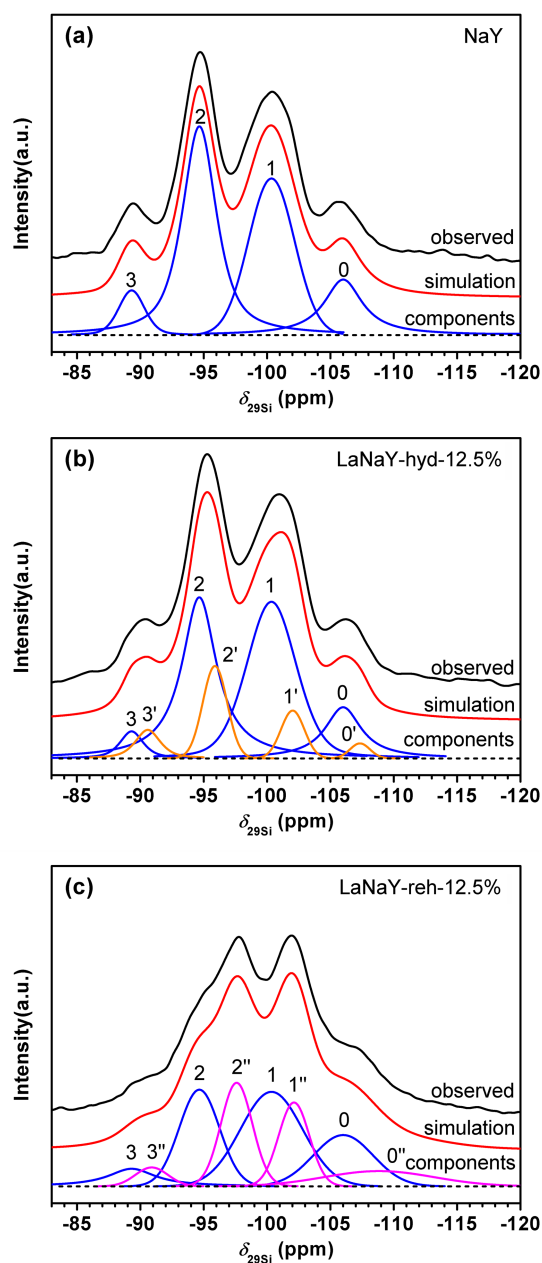


Fig. S8 Deconvolution results of ^{29}Si MAS NMR spectra of (a) NaY, (b) LaNaY-hyd-12.5%, and (c) LaNaY-reh-12.5%.

References

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