Supporting Information for

Revealing the evolution of local structure in the formation process of alkaline earth metal cation-containing zeolite from glass

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Additional simulation details

Reverse Monte Carlo (RMC) simulation of Ba- and Ca-containing glasses

The RMC simulation was performed using the RMC_POT program constrained by the experimental structural data, the cut-off interatomic distances and the coordination numbers.[1] The simulation box contained 10000 atoms with the number density of 0.050 and 0.064 atom $Å^{-3}$ for Ba-glass and Ca-glass, respectively. The cut-off interatomic distances for each atom pair were set as the following tables (unit: Å). For Ba-glass, each Si atom was forced to be surrounded by four O neighbors between 1.4 and 1.8 Å, and each Al atom was forced to have four O neighbors between 1.5 and 1.8 Å. For Ca-glass, each Si atom was forced to be surrounded by four O neighbors between 1.4 and 2.0 Å, and each Al atom was forced to have four O neighbors between 1.5 and 2.0 Å. For both glasses, each O atom was forced to have at most two Si/Al neighbors between the corresponding limits. The constraints were fulfilled for the corresponding atoms by 93% and 96% for Ba-glass and Ca-glass, respectively.

(a) Ba-glass

	Si	Al	Ba	O
Si	2.6	2.6	3.3	1.3
Al	–	2.5	3.3	1.4
Ba	–	–	3.8	2.5
O	–	–	–	2.2

(b) Ca-glass

	Si	Al	Ca	O
Si	2.6	2.6	2.6	1.4
Al	–	2.5	2.6	1.5
Ca	–	–	2.8	2.2
O	–	–	–	2.2

Simulated reduced pair distribution function of harmotome and Phillipsite-Ca

The simulation was conducted by software *PDFgui*.[2] The structural models of harmotome and Phillipsite-Ca were created based on the previously published crystallographic information files,[3,4] and that of harmotome was further modified to fit the experimental scattering data. Here, the framework was assumed to be composed of only Si and O.[5] The software *VESTA* was used to visualize the structural models.[6]

Supplementary Tables

Table S1 Summary of the zeolites that have not been artificially synthesized and their extra-framework cations (the alkaline earth metal cations are highlighted)

Structure code	Name	Extra-framework cation
AFG	Afghanite	Na, K, **Ca**
BCT	Svyatoslavite	**Ca**
-CHI	Chiavennite	**Ca**, Mn
DAC	Dachiardite	**Ca**, Na, K
FAR	Farneseite	**Ca**, Na, K
FRA	Franzinite	Na, K, **Ca**
GIU	Giuseppettite	Na, K, **Ca**
GOO	Goosecreekite	**Ca**
LIO	Liottite	Na, **Ca**
MAR	Marinellite	Na, **Ca**
MON	Montesommaite	K, Na
NAB	Nabesite	Na
-PAR	Partheite	**Ca**
-RON	Roggianite	**Ca**
TER	Terranovaite	Na, **Ca**
TOL	Tounkite-like material	Na, **Ca**, K
TSC	Tschornerite	**Ca**, **Sr**, K, **Ba**
WEI	Weinebeneite	**Ca**
-WEN	Wenkite	**Ba**, **Ca**, Na

Table S2 Solubility of different hydroxides in water at 25 °C[7,8]

Hydroxide	Solubility (g/100 g H_2O)
LiOH	12.8
NaOH	114
KOH	118
CsOH	400
$Mg(OH)_2$	0.001
$Ca(OH)_2$	0.150
$Sr(OH)_2$	1.00
$Ba(OH)_2$	4.54

Supplementary Figures

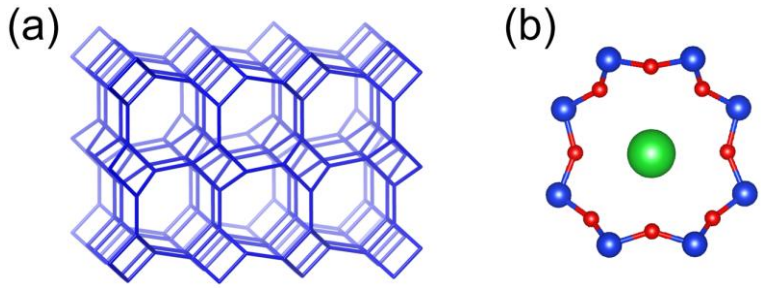

Fig. S1 (a) PHI-type topological structure viewed along **a**-axis. (b) Symmetric Ba-containing 8R in harmotome. Blue: T (Si or Al); red: O; green: Ba. The PHI framework is comprised of 4Rs and 8Rs. The chains of the doubly connected 4Rs (known as double crankshafts) run parallel to the **a**-axis. Three types of channels confined by 8Rs exist, parallel to the **a**-, **b**- and **c**-axes, respectively. The Ba^{2+} cations in the harmotome are coordinated by the 8Rs aligned along the **c**-axis. The projections of the PHI-type topological structure along each axis can be found in **Fig. S10**.

Fig. S2 Photo of the carbon-coated reactor. Due to the small amount of the reactant in each batch of the synthesis, this small reactor is employed, where the carbon coating plays a role same as the Teflon cup in the conventional autoclave.

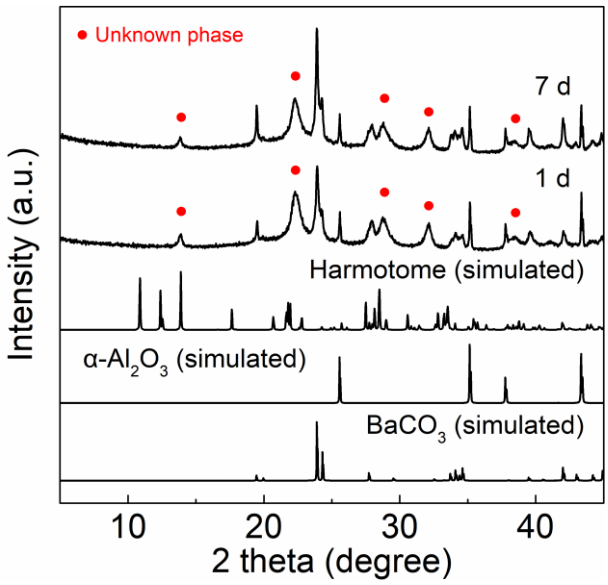

Fig. S3 XRD patterns of the products synthesized from Ba-PM for 1 d and 7 d (referenced with simulated XRD patterns of $BaCO_3$, Al_2O_3 and harmotome).

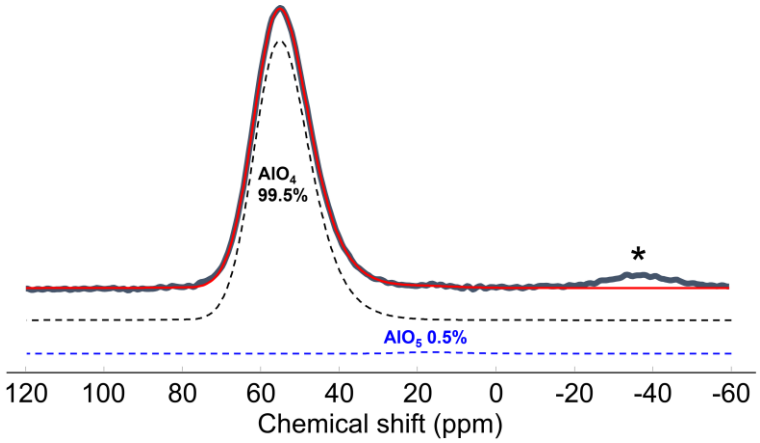

Fig. S4 ^{27}Al MAS NMR spectrum of Ba-glass acquired at 18.79 T. The spectrum was fitted by software *dmfit*. The asterisk donates the spinning sideband.

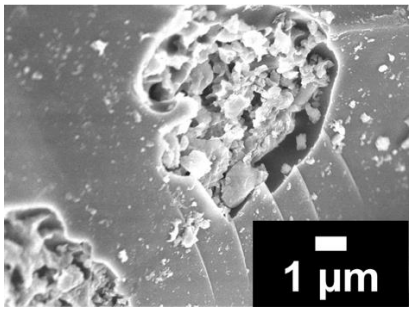

Fig. S5 FE-SEM image of the product synthesized from Ba-glass for 1 d, showing the severely etched surface.

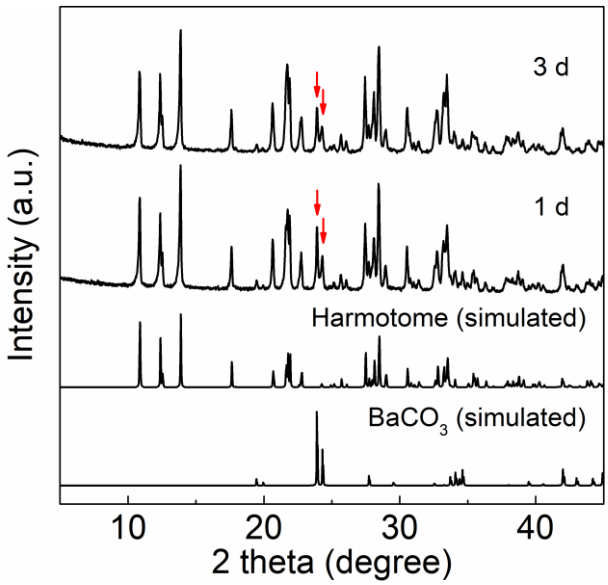

Fig. S6 XRD patterns of the products synthesized from Ba-glass for 1 d and 3 d in a pH 14 NaOH solution (referenced with simulated XRD patterns of $BaCO_3$ and harmotome). The red arrows indicate the diffraction peaks derived from $BaCO_3$.

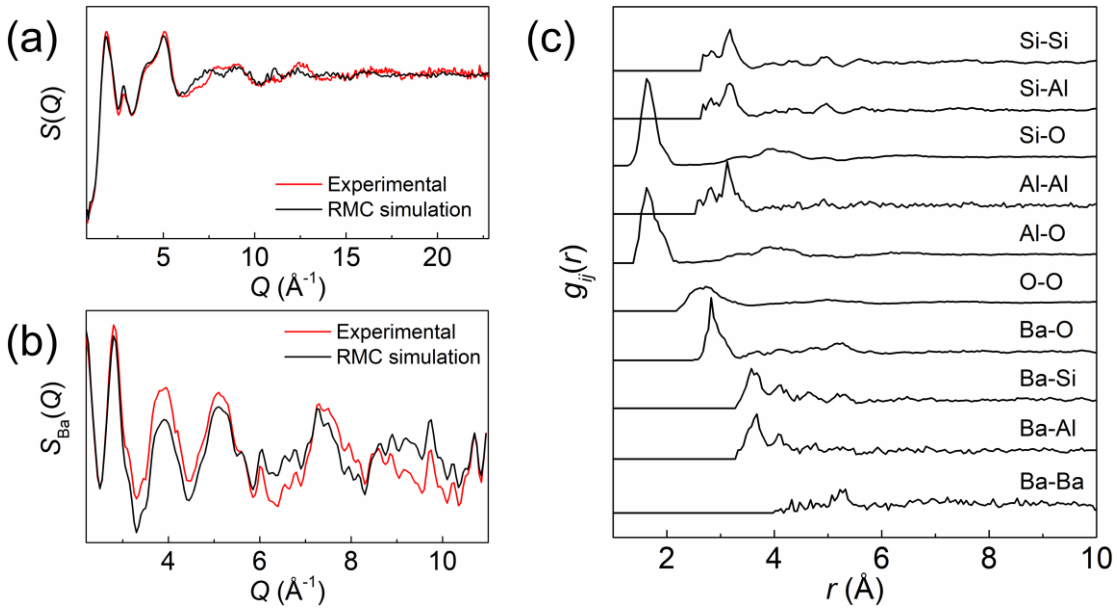

Fig. S7 Comparison of (a) total structure factors, $S(Q)$, and (b) differential structure factors, $S_{Ba}(Q)$, of Ba-glass obtained by experimental measurement and RMC simulation. (c) Partial PDFs, $g_{ij}(r)$, of Ba-glass obtained by RMC simulation.

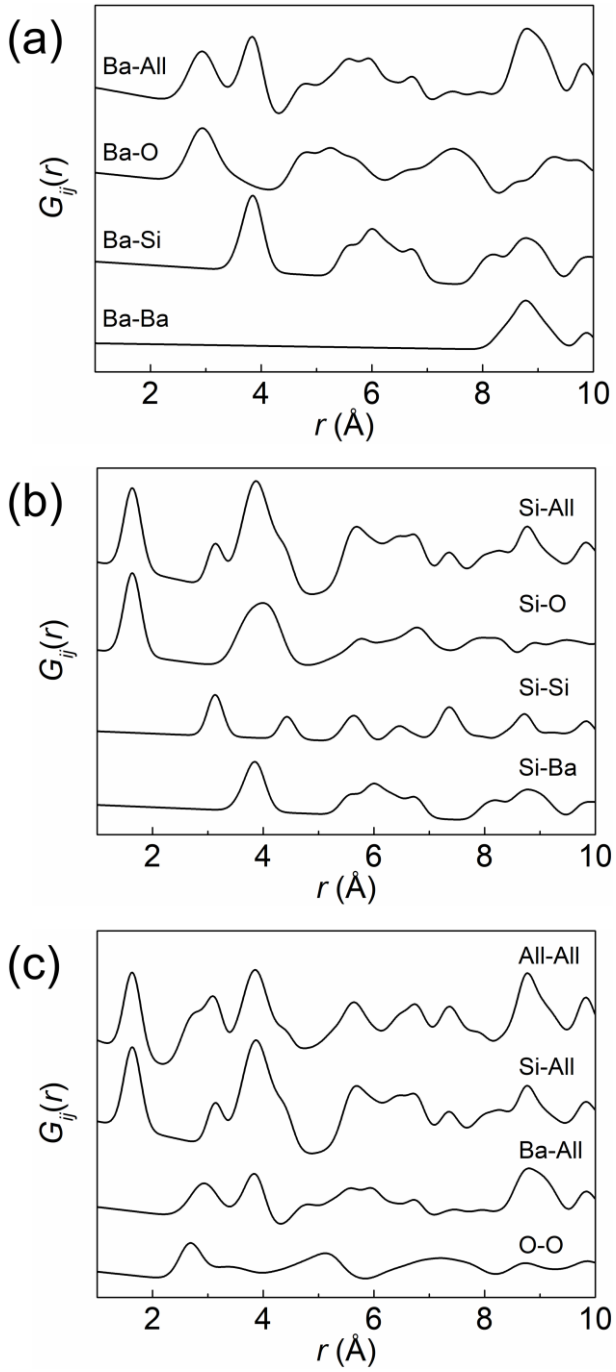

Fig. S8 Partial reduced PDFs, $G_{ij}(r)$, of harmotome obtained by software *PDFgui*. (a) and (b) show all the $G_{ij}(r)$ related to Ba and Si, respectively, where Ba–All and Si–All mean the sum of each $G_{ij}(r)$ related to Ba and Si, respectively. In (c), All–All means the total reduced PDF, $G(r)$, of harmotome.

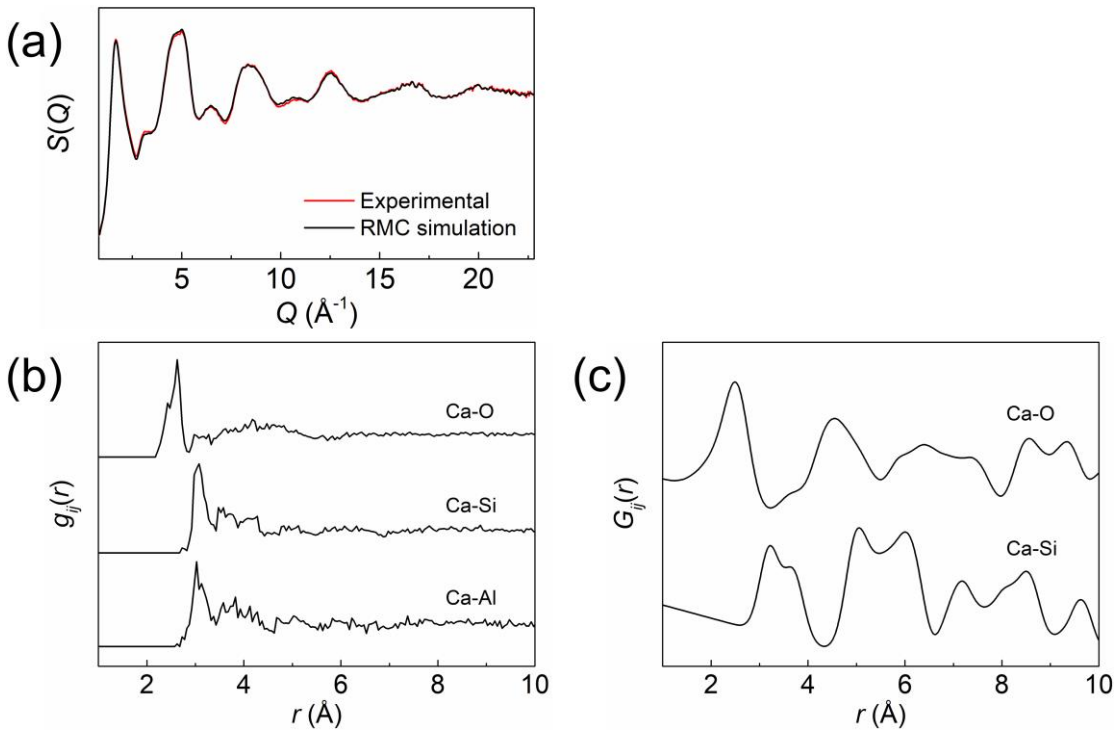

Fig. S9 (a) Comparison of total structure factors, $S(Q)$, of Ca-glass obtained by experimental measurement and RMC simulation. (b) Partial PDFs, $g_{ij}(r)$, of Ca–O/Si/Al pairs of Ca-glass obtained by RMC simulation. (c) Partial reduced PDFs, $G_{ij}(r)$, of Ca–O/Si pairs of Phillipsite-Ca obtained by software *PDFgui*.

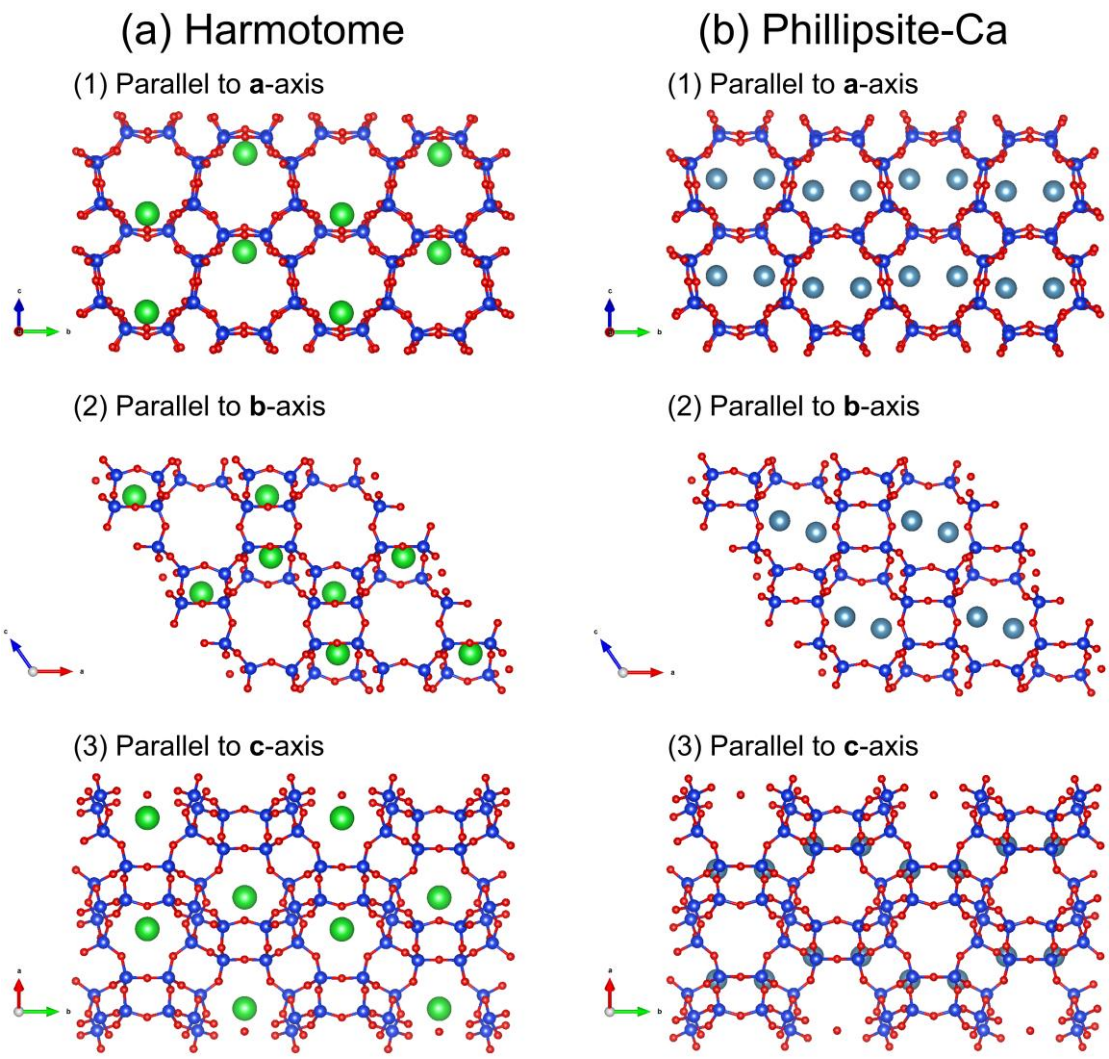

Fig. S10 Illustrations of (a) Ba^{2+} sites in harmotome and (b) Ca^{2+} sites in Phillipsite-Ca. Ba^{2+} cations in the harmotome block the 8R channels parallel to the **c**-axis, while Ca^{2+} cations in the Phillipsite-Ca obstruct the 8R channels parallel to the **a**- and **b**-axes.[9]

References

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