

# Supplementary Material

for

## Sol-gel synthesis and characterization of lithium aluminate (L–A–H) and lithium aluminosilicate (L–A–S–H) gels

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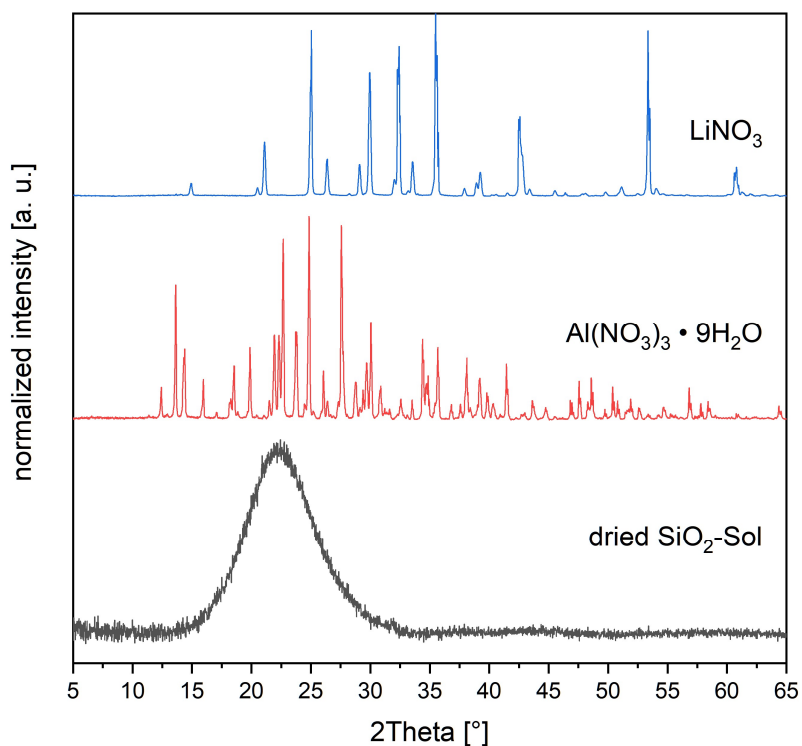
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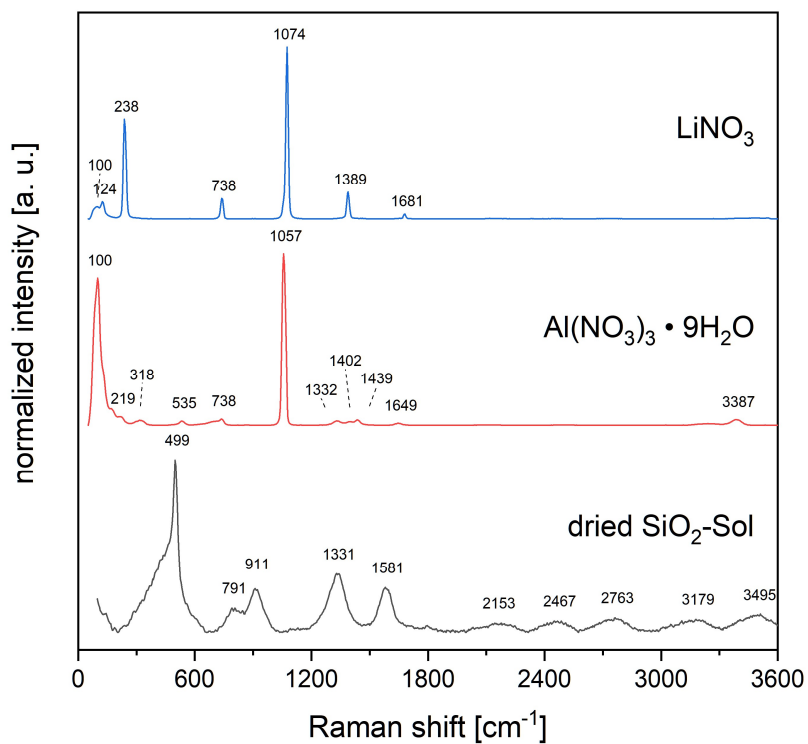
### **This PDF file includes:**

Supplementary Figures S1–S6

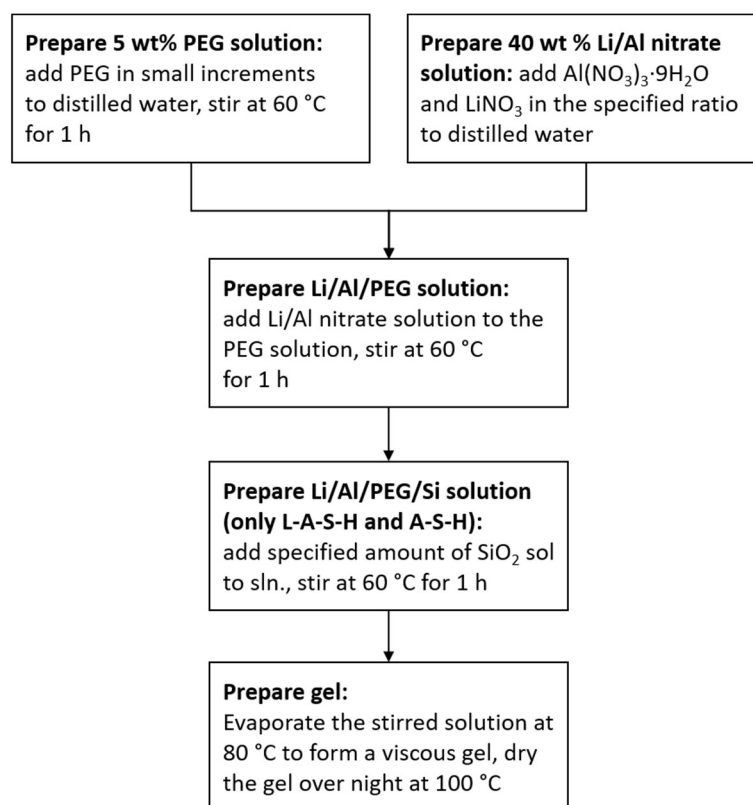
Supplementary Tables S1–S3



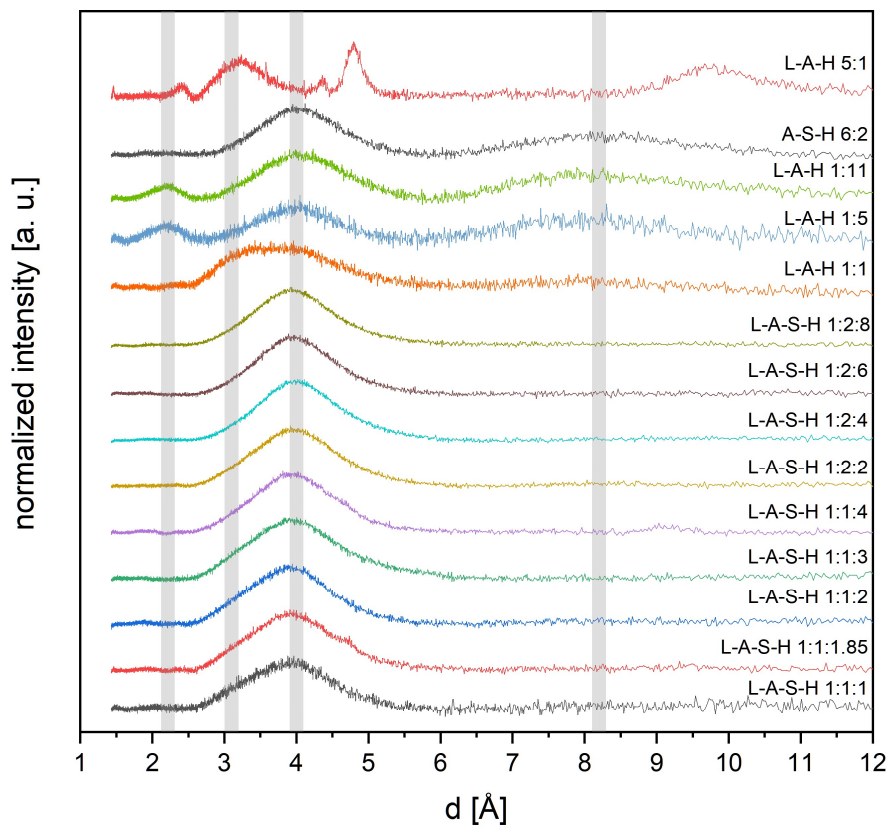
**Supplementary Figure S1.** XRD patterns of the starting materials  $\text{LiNO}_3$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and the colloidal silica ( $\text{SiO}_2$  sol). The colloidal silica was dried at 80 °C for 24 h before the measurement.



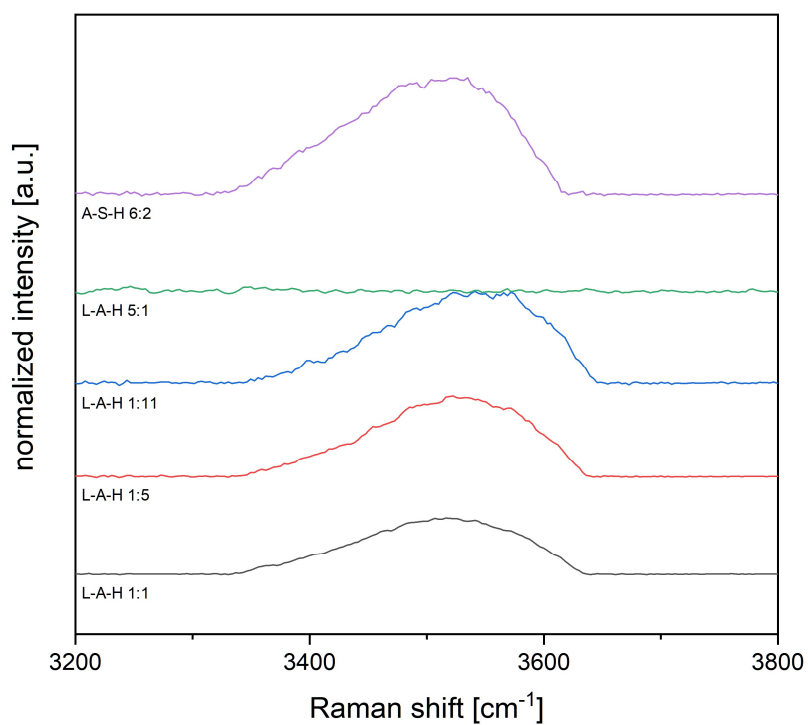
**Supplementary Figure S2.** Raman spectra of the starting materials  $\text{LiNO}_3$ ,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , and the colloidal silica ( $\text{SiO}_2$  sol). The colloidal silica was dried at 80 °C for 24 h before the measurement.



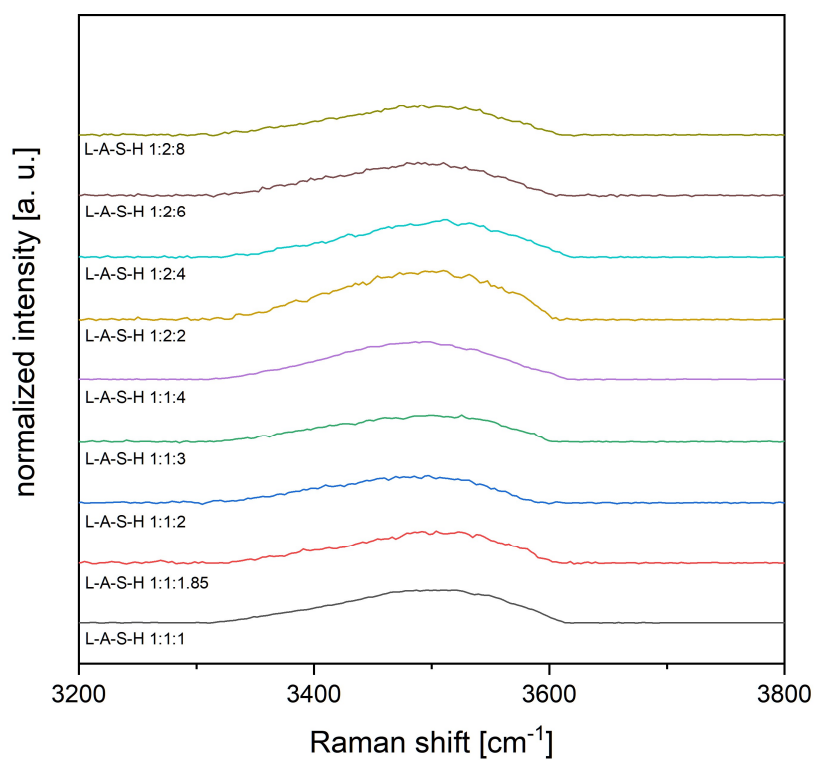
**Supplementary Figure S3.** Flow chart of the organic steric entrapment route, modified to synthesize the L–A–S–H, L–A–H and A–S–H gels. For the synthesis of the L–A–H gels, addition of the SiO<sub>2</sub> sol was omitted; for the synthesis of the A–S–H gel, the starting Li/Al solution was prepared with only Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (no LiNO<sub>3</sub>).



**Supplementary Figure S4.** Background-corrected and normalized XRD patterns of the gels. The grey bars indicate  $d$ -spacings of approximately 2.2, 3.1, 4.0 and 8.2 Å, respectively.



**Supplementary Figure S5.** Background-corrected and normalized Raman spectra of the L–A–H gels and the A–S–H gel in the range 3200–3800  $\text{cm}^{-1}$  (water and hydroxyl stretching).



**Supplementary Figure S6.** Background-corrected and normalized Raman spectra of the L–A–S–H gels in the range 3200–3800  $\text{cm}^{-1}$  (water and hydroxyl stretching).

**Supplementary Table S1.** Isotropic chemical shifts and integrated intensities of the  $\text{AlO}_6$  and  $\text{AlO}_5$  resonances observed in the  $^{27}\text{Al}$  MAS NMR spectra (field strength 17.6 T) of the gels. The designations of the resonances in the header row indicate the model applied to fit the resonances and, for the resonances fitted with a Gaussian function, their approximate chemical shift.

Sample	Czjzek	Gauss 10	Gauss 32
L-A-H 5:1	17.9 ppm	~10 ppm (53.9%) <sup>a</sup>	* <sup>b</sup>
A-S-H 6:2	11.4 ppm	-	32.5 ppm (3.7%)
L-A-H 1:11	11.7 ppm	-	33.9 ppm (4.1%)
L-A-H 1:5	11.9 ppm	-	32.1 ppm (3.9%)
L-A-H 1:1	11.9 ppm	-	33.4 ppm (2.3 %)
L-A-S-H 1:2:8	9.9 ppm	-	34.5 ppm (2.0%)
L-A-S-H 1:2:6	8.0 ppm	10.5 ppm (4.2%)	*
L-A-S-H 1:2:4	11.9 ppm	-	34.4 ppm (2.6%)
L-A-S-H 1:2:2	11.8 ppm	-	34.5 ppm (1.6%)
L-A-S-H 1:1:4	9.1 ppm	11.3 ppm (6.4 %)	36.0 ppm (2.0%)
L-A-S-H 1:1:3	12.5 ppm	-	32.3 ppm (2.4%)
L-A-S-H 1:1:2	2.6 ppm	10.0 ppm (54.5%)	36.8 ppm (0.1%)
L-A-S-H 1:1:1.85	3.8 ppm	10.0 ppm (37.7%)	*
L-A-S-H 1:1:1	11.8 ppm	-	34.8 ppm (1.7%)

<sup>a</sup> Resonance fitted with two Gaussian functions, centred at 9.9 ppm (37.0 %) and 8.4 ppm (16.9 %), respectively.

<sup>b</sup> An asterisk (\*) indicates that a minor, non-quantifiable resonance might be present.

**Supplementary Table S2.** Isotropic chemical shifts and integrated intensities of the Q<sup>4</sup>, Q<sup>3</sup> and Q<sup>2</sup> resonances observed in the <sup>29</sup>Si MAS NMR spectra of the L–A–S–H gels. The designations of the resonances in the header row indicate the species and their approximate chemical shift (centre).

<b>Sample</b>	<b>Q4 –112</b>	<b>Q3 –102</b>	<b>Q2 –95</b>
L-A-S-H 1:2:8	–111.7 ppm (82.0 %)	–102.0 ppm (18.0 %)	-
L-A-S-H 1:2:4	–111.5 ppm (83.7 %)	–102.0 ppm (13.1 %)	–95.8 ppm (3.3 %)
L-A-S-H 1:2:2	–111.5 ppm (84.3 %)	–102.0 ppm (10.2 %)	–95.8 ppm (5.5 %)
L-A-S-H 1:1:4	–111.5 ppm (85.3 %)	–101.7 ppm (14.7 %)	-
L-A-S-H 1:1:2	–111.6 ppm (78.6 %)	–101.9 ppm (19.8 %)	–92.0 ppm (1.6 %)
L-A-S-H 1:1:1	–111.5 ppm (89.0 %)	–99.9 ppm (11.0 %)	-

**Supplementary Table S3.** Spectral ranges of Raman bands with their assignments to structural units in silicate and aluminosilicate glasses, hydrous semi-crystalline silicates and aluminosilicates, and hydrous semi-crystalline and crystalline aluminates.

<b>Spectral range (cm<sup>-1</sup>)</b>	<b>Structural unit</b>	<b>Vibration</b>	<b>References<sup>a</sup></b>
430–500	SiO <sub>2</sub> /Q <sup>4</sup>	Si–O symmetric stretching	Sharma et al. 1981; McMillan 1984
~440	AlO <sub>4</sub> <sup>5-</sup>	Al–O stretching	Watling et al. 1999
490–550	AlO <sub>6</sub> <sup>9-</sup>	Al–O stretching	Watling et al. 1999; Renaudin et al. 2007; Torr�ns-Martin et al. 2013
580–630	Si <sub>2</sub> O <sub>5</sub> <sup>2-</sup> /Q <sup>3</sup>	Si–O–Si motion (incl. bending)	McMillan 1984; Mysen et al. 1985; Kirkpatrick et al. 1997
620–680	Si <sub>2</sub> O <sub>6</sub> <sup>4-</sup> /Q <sup>2</sup>	Si–O–Si motion (incl. bending)	McMillan 1984; Mysen et al. 1985; Kirkpatrick et al. 1997; Renaudin et al. 2009; Ortaboy et al. 2017
~700	Si <sub>2</sub> O <sub>7</sub> <sup>6-</sup> /Q <sup>1</sup>	Si–O–Si motion (incl. bending)	McMillan 1984; Mysen et al. 1985
710–730	NO <sub>3</sub> <sup>-</sup>	N–O degenerate symmetric stretching/planar angular deformation	Kloprogge and Frost 1999; Renaudin et al. 2000
830–860	SiO <sub>4</sub> <sup>4-</sup> /Q <sup>0</sup>	Si–O symmetric stretching	McMillan 1984; Nesbitt et al. 2017; Ortaboy et al. 2017
880–910	Si <sub>2</sub> O <sub>7</sub> <sup>6-</sup> /Q <sup>1</sup>	Si–O symmetric stretching	McMillan 1984; Mysen et al. 1985; Kirkpatrick et al. 1997; Garbev et al. 2007; Renaudin et al. 2009; Ortaboy et al. 2017; Nesbitt et al. 2017
~890	Si(OAl) <sub>4</sub> /Q <sup>4</sup> (4Al)	(Si,Al)–O stretching	McMillan et al. 1982



940–1010	Si <sub>2</sub> O <sub>6</sub> <sup>4-</sup> /Q <sup>2</sup>	Si–O symmetric stretching	McMillan 1984; Mysen et al. 1985; Kirkpatrick et al. 1997; Garbev et al. 2007; Renaudin et al. 2009; Nesbitt et al. 2017
~925	(SiO) <sub>–</sub> Si(OAl) <sub>3</sub> / Q <sup>4</sup> (3Al)	(Si,Al)–O stretching	McMillan et al. 1982; McMillan and Piriou 1982
~1000	(SiO) <sub>2–</sub> Si(OAl) <sub>2</sub> / Q <sup>4</sup> (2Al)	(Si,Al)–O stretching	McMillan et al. 1982
1040–1070	NO <sub>3</sub> <sup>–</sup>	N–O symmetric stretching	Kloprogge and Frost 1999; Renaudin et al. 2000
1050–1100	Si <sub>2</sub> O <sub>5</sub> <sup>2-</sup> /Q <sup>3</sup>	Si–O symmetric stretching	McMillan 1984; Mysen et al. 1985; Kirkpatrick et al. 1997; Renaudin et al. 2009; Ortaboy et al. 2017; Nesbitt et al. 2017
~1060 (weak)	SiO <sub>2</sub> /Q <sup>4</sup>	Si–O asymmetric stretching	McMillan 1984
1070–1085	CO <sub>3</sub> <sup>2-</sup>	C–O symmetric stretching	Kirkpatrick et al. 1997; Martinez-Ramirez et al. 2003; Renaudin et al. 2009; Ortaboy et al. 2017
~1140	(SiO) <sub>3–</sub> Si(OAl)/ Q <sup>4</sup> (1Al)	(Si,Al)–O stretching	McMillan et al. 1982
1190–1250 (weak)	SiO <sub>2</sub> /Q <sup>4</sup>	Si–O asymmetric stretching	McMillan 1984; Nesbitt et al. 2017
1340–1385	NO <sub>3</sub> <sup>–</sup>	N–O asymmetric stretching	Kloprogge and Frost 1999

<sup>a</sup> References to Supplementary Table S3:

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