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Supplementary Information

for

NMR Studies of Li Mobility in NASICON-Type Glass-Ceramic Ionic Conductors with Optimized Microstructure

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1. Pseudo-Voigt function for fitting the central line of the ^{7}Li NMR spectra

$$V_P(x) = A \cdot \left[R \frac{2}{\pi} \frac{\sigma_{PV}}{4(x-\mu)^2+\sigma_{PV}^2} + (1-R) \frac{\sqrt{4\ln(2)}}{\sigma_{PV}\pi^{\frac{1}{2}}} \cdot \exp\left(-4\ln(2)\frac{x-\mu^2}{\sigma_{PV}}\right) \right],$$

where R is a weighting factor, σ_{PV} is the full width at half maximum and μ is a displacement of the maximum relative to 0.

2. Analysis of experimental and theoretical second moments of the linewidths for LAGP and LAGPY.

Theoretical second moment values have been found using homonuclear and heteronuclear atomic distances applying the formulas given in the Abragam's book (Abragam, A. "The principles of nuclear magnetism" Oxford: Oxford Univ. Press, 1961). Four crystal structure data files refined from neutron diffraction measurements have been considered after relaxing the atomic positions to forces less than 10^{-3} eVÅ^{-1} by means of DFT: one for LAGP and three for LAGPY, where various sites were taken into account for Al substitution. The experimental second moment values M_2 have been calculated from the full width at half maximum σ_{PV} of the spectral fit using the pseudo-Voigt function: $M_2 = \frac{\sigma_{PV}^2}{2*\sqrt{2ln2}} = \frac{\sigma_{PV}^2}{5.54}$.

Table S1. Calculated and experimental second moment values in the rigid lattice regime.

	LAGP		LAGPY[a)]					
			I-Y		II-Y		III-Y	
	r, Å	M_2, 10^6 Hz^2	r, Å	M_2, 10^6 Hz^2	r, Å	M_2, 10^6 Hz^2	r, Å	M_2, 10^6 Hz^2
Li1-Li3	3.40	1.21	4.58	0.20	4.61	0.19	4.64	0.19
Li1-P	2.71	0.28	3.16	0.11	3.30	0.09	3.25	0.10
Li3-P	3.09	0.13	2.94	0.18	2.65	0.33	2.60	0.36
Li1-Al	-	-	4.64	0.10	4.71	0.09	4.72	0.09
Li3-Al	-	-	3.18	0.98	2.94	1.57	7.12	0.08
Exp. M_2, 10^6 Hz^2	-	2.1	-	-	-	1.5	-	-

a) For LAGPY two structures have been calculated in addition, in which an additional Al atom in two different positions is considered.

3. XRD analysis of precursor glasses

X-ray diffraction (XRD) patterns were recorded using Bruker D8 Advance diffractometer with reflective Bragg-Brentano geometry using Cu Kα radiation in the 2θ range from 10° to 90° with a step width of 0.02°. XRD patterns presented in Fig. S1 indicate no signs of crystalline species.

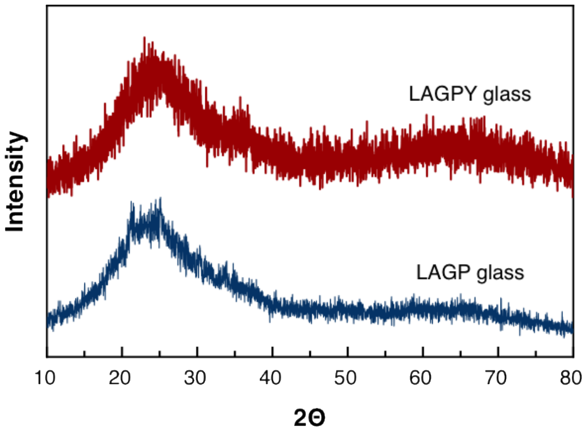

Figure S1. XRD patterns for starting glassy materials with Y_2O_3 adding (on the top) and without (on the bottom) after grinding for NMR measurements.

4. DFT calculations of total energies and NMR parameters.

Three structural arrangements were modelled for each sample to account for incomplete occupancy of Li and Al sites. Since in particular the specific location of Al influences the determined electric field gradients (EFGs), Figure S2 exemplarily demonstrates the structural differences for location Al1 (arrangement II-Y, without Li "on-top" position) and Al2 (arrangement III-Y, with Li "on-top" position) of the Y-modified samples. Our first-principle calculations of the total energy values, quadrupolar coupling constants, and asymmetry parameters are presented in Tables S2 and S3 for LAGP and LAGPY, respectively. ^{7}Li quadrupolar coupling constants C_Q calculated from EFGs of Li1 close to Li3 are increased to in average 30 kHz (see arrangements II and II-Y in Tables S2 and S3) as compared to the "normal" position far from Li3 with in average 16 kHz. Furthermore, due to the local atomic arrangement, the C_Q values are increased for Li1 in "in-plane" position to Al (in average 28 kHz) and for Li3 if Al is located in second coordination shell (88 vs in average 68 kHz) and decreased for Li1 in "on-top" position (4 kHz).

In order to demonstrate that the experimentally observed low-temperature line shape is a superposition of various Pake patterns associated with Li sites with different local symmetry due to the structural distribution, we have simulated the theoretical spectrum based on DFT calculations of electrical field gradients. Figure S3 shows the experimental spectrum of LAGPY at temperature of 92 K together with the calculated spectrum for a half cell of LAGPY, which comprised seven Li sites. The results show that all ^{7}Li have the different C_Q values caused by differences in local environments due to incomplete occupancy of Li and Al sites. From symmetry considerations (local ^{7}Li coordination), these Li sites can be grouped in Li1 and Li3 sites indicating the higher C_Q values for Li3. It is obvious that a superposition of seven line shapes with even a slight broadening (red line in Figure S3) does not represent a Pake shape. The discrepancy with the experimental spectrum can be related to the computational limitations and the number of the Li atoms in the calculated cell. In our previous publication (A. Vyalikh *et al,* Phys Rev Mater, 2018, 2, 013804) we have demonstrated sensitivity of the calculated ^{7}Li EFG to the boundary conditions of crystal defect models.

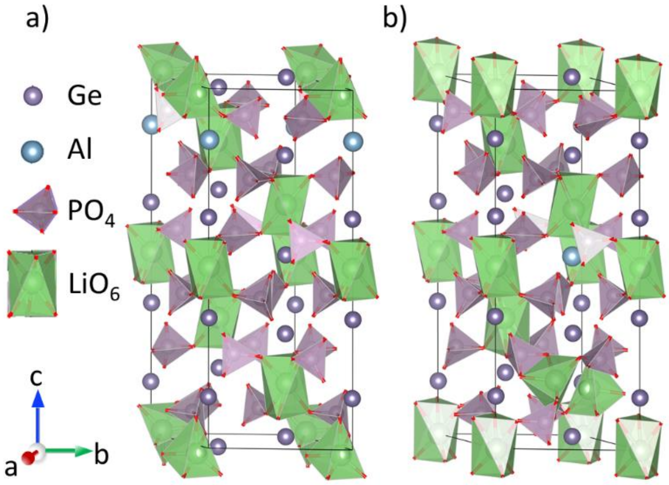

Figure S2. DFT-relaxed LAGPY crystal structures of Rietveld refined neutron powder diffraction data for two different arrangements of Al (blue sphere) on the Ge positions (a) with and (b) without Li in “on-top” position, corresponding to the arrangements II-Y and III-Y in Table S3, respectively.

Table S2. DFT calculated parameters (total energy E_{tot} (eV), quadrupolar coupling constant C_Q (kHz) and asymmetry parameter η) for different structural arrangements (I-III) in LAGP.

	I				II				III			
	C_Q	η	C_Q	η	C_Q	η	C_Q	η	C_Q	η	C_Q	η
Li1	44	1.0			22	0.3			30 $^{b)}$	0.4		
	26	0.4			18	0.7			13	0.9		
	38	0.5			31 $^{a),b)}$	0.2			27 $^{a)}$	0.4		
	50	0.2			17	0.7			10 $^{c)}$	1.0		
	10	0.5			44 $^{a)}$	0.3			26 $^{a)}$	0.3		
Li3			70	0.9			87 $^{d)}$	0.5			68	0.5
			51	0.8			65	0.7			66	0.5
Aver.	34		61		26		76		21		67	
E_{tot}	-748.12				-753.47				-753.05			

$^{a)}$ Li1 close to Li3; $^{b)}$ Li1 in “in-plane” position to Al; $^{c)}$ Li1 in “on-top” position to Al;

$^{d)}$ Li3 close to Al

Table S3. DFT calculated parameters (total energy E_{tot} (eV), quadrupolar coupling constant C_Q (kHz) and asymmetry parameter η) for different structural arrangements (I-Y, II-Y and III-Y) in LAGPY.

	I-Y				II-Y				III-Y			
	C_Q	η	C_Q	η	C_Q	η	C_Q	η	C_Q	η	C_Q	η
Li1	24	0.2			17	0.4			29 $^{a)}$	0.1		
	24	0.1			13	0.8			19 $^{b)}$	0.3		
	31	0.6			30 $^{a),b)}$	0.2			21 $^{a)}$	0.6		
					14	0.7			18	0.2		
					40 $^{a)}$	0.2			4 $^{c)}$	0.5		
Li3			61	0.8			88 $^{d)}$	0.5			77	0.4
			67	0.4			66	0.7			67	0.4
Aver.	26		64		23		77		18		72	
E_{tot}	-744.64				-753.49				-752.97			

$^{a)}$ Li1 close to Li3; $^{b)}$ Li1 in “in-plane” position to Al; $^{c)}$ Li1 in “on-top” position to Al;

$^{d)}$ Li3 close to Al

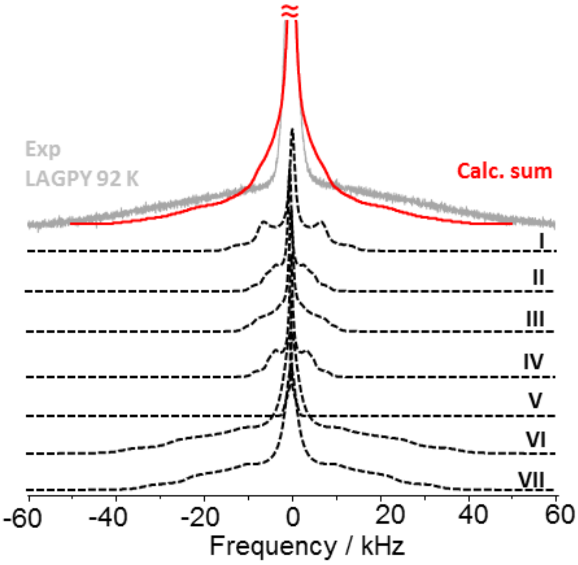

Figure S3. Simulated ^{7}Li NMR spectrum for a half cell of LAGPY (red line), which comprised seven Li sites denoted by I to VII (black dashed lines). The experimental spectrum is shown by solid grey line.

5. *Field-Cycling Relaxometry*

Figure S4 displays the dispersions $T_1^{-1}(\nu_0)$ obtained from ^{7}Li FC relaxometry at various temperatures. We see that the frequency dependence of T_1^{-1} is weak in the whole range and low- or high-frequency plateaus of the spin-lattice relaxation rates are not reached in the accessible frequency and temperature ranges. Hence, our measurements of $T_1^{-1}(\nu_0)$ reveal that Li dynamics in LAGPY is characterized by strongly nonexponential correlation functions, suggesting that broad distributions of correlation times exist.

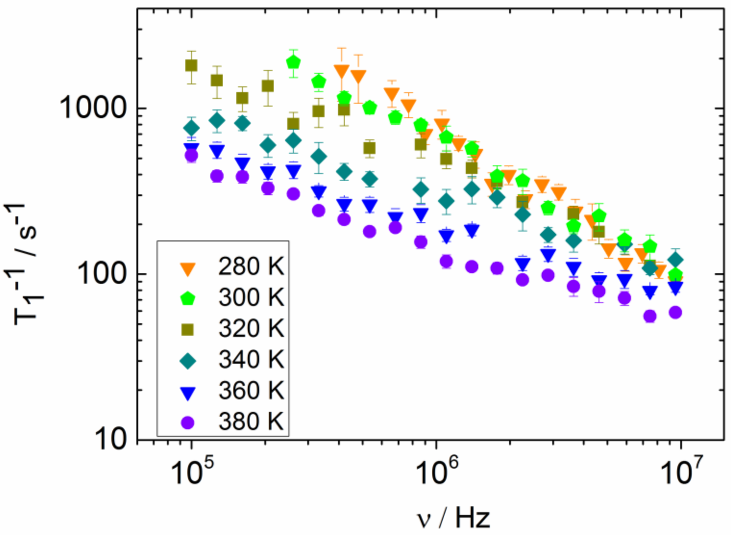

Figure S4. Frequency dependence of T_1^{-1} for LAGPY at various temperatures as obtained from ^{7}Li field-cycling relaxometry.