Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2023

Electronic Supplementary Information

Influence of synthesis and substitution on the structure and ionic transport properties of lithium rare earth metal halides

Maximilian A. Plass,^{*a*, *b*} Sebastian Bette,^{*a*} Nina Philipp,^{*a*, *b*} Igor Moundrakovski,^{*a*} Kathrin Küster,^{*a*} Robert E. Dinnebier,^{*a*} Bettina V. Lotsch^{*, *a*, *b*}

^a Max-Planck-Institute for Solid State Research, HeisenbergstraSSe 1, 70569 Stuttgart, Germany
 ^b Ludwig-Maximilians University, ButenandtstraSSe 5-13, 81377 München, Germany

E-Mail: b.lotsch@fkf.mpg.de

Contents

Synthesis	2
X-Ray Diffraction Analysis	4
X-Ray Photoelectron Spectroscopy	12
Solid-State NMR	12
Electrochemical Impedance Spectroscopy	16
Bond Valence Sum Calculations	26
Pulsed-Field-Gradient NMR	27

Synthesis

The conventional solid-state synthesis (SSS) of the lithium rare earth iodides Li_3MI_6 with M = Y, Sm, Gd-Lu was carried out starting from stoichiometric amounts of LiI (99.95%, anhydrous, ALFA AESAR) and the respective M_{I_3} . To this end, the starting materials were ground in an agate mortar in an argon-glovebox, filled into glassy carbon crucibles, transferred into quartz glass ampoules, and sealed under dynamic vacuum. Instead, Li_3SmI_6 was synthesized starting from SmI₂, LiI, and I₂ (sublimed, MERCK). The di- and trihalides of the rare earth (RE) metals $(SmI_2, MI_3 \text{ with } M = Y, Gd-Lu \text{ and } YBr_3)$ were synthesized from RE metals M and I₂ or from M_2O_3 and NH_4X with X = Br or I as described elsewhere.¹ The quartz ampoules were heated under dynamic vacuum using a blow torch and flushed with argon for several times to remove traces of O₂ and H₂O before using them. The loaded quartz ampoules were heated to a certain temperature (see Tab. S1) with a rate of $100 \,^{\circ}\mathrm{Ch}^{-1}$ and held for 24 h. The reaction mixtures were also cooled down with a rate of $100 \,^{\circ}\mathrm{C}\,\mathrm{h}^{-1}$. Partial aliovalent cation substitution in $\text{Li}_{3+y}\text{Gd}_{1-y}\text{Cd}_y\text{I}_6$ with y = 0.05, 0.1, 0.25, 0.5 and 0.75 was tested by reacting stoichiometric amounts of GdI_3 , LiI and CdI_2 the same way as described for Li_3MI_6 . CdI_2 was synthesized from Cd (granules, 99.999%, Aldrich) and a small excess of I_2 in an ampoule, which were cooled with liquid nitrogen during evacuating and sealing. The loaded quartz ampoules were heated to $350\,^{\circ}\text{C}$ with a rate of $100 \,\mathrm{K \, h^{-1}}$ for 55 h and afterwards quenched in water with one end first to remove excess of I₂ from the product. Furthermore, $\text{Li}_3 \text{YBr}_{3.5} \text{I}_{2.5}$ and $\text{Li}_{3+y} \text{Y}_{1-y} M^{II}_y \text{Br}_{3.5} \text{I}_{2.5}$ with

 $M^{II} = Cd$, Ca and $Li_{3-y}Y_{1-y}M^{IV}{}_{y}Br_{3.5}I_{2.5}$ with $M^{IV} = Zr$, all with y = 0.1, were synthesized like the other $Li_{3}MI_{6}$ and $Li_{3}HoBr_{6-x}I_{x}{}^{2}$ phases starting from stoichiometric amounts of LiBr, LiI, YBr₃ and CdI₂, CaI₂ (powder, 99.99%, ALFA AESAR) or ZrI₄, respectively, at 666 °C for 60 h using a rate of 50 K h⁻¹ for heating and cooling. ZrI₄ was synthesized from Zr (powder, -100 mesh, dried, ALDRICH) and I₂, similar to CdI₂, at 500 °C with a rate of 100 K h⁻¹ for 24 h. For comparison Li₃YBr₆ was synthesized according to a similar method as described for Li₃HoBr₆.² In addition, Li₃YI₆ and Li₃TmI₆ were synthesized *via* mechanochemical mechanochemical ballmilling (MCBM) in a mixing mill (RETSCH MM 400). Here, the same precursors as used for the SSS were filled into zirconia beakers with a volume of 10 mL. The milling procedure was performed stepwise, starting with 10.5 h at a frequency of 10 Hz and three zirconia balls with a diameter of 5 mm. After increasing the frequency to 15 Hz for 6 h, the 5 mm zirconia balls were replaced with one having a diameter of 10 mm and the reaction mixtures were shaken for 4.5 h and 9 h at a frequency of 30 Hz. Powder of the last MCBM iteration was also sealed in a quartz ampoule the same way as for the SSS, annealed at 500 °C for 60 h and cooled with a rate of 50 K h^{-1} .

M in Li ₃ M I ₆	rate $[{\rm K}{\rm h}^{-1}]$	$T \ [^{\circ}C]$	dwell [h]
Sm	100	500	24
Gd	100	700	24
Tb	100	750	24
Dy	100	750	24
Но	100	750	24
Y(LT)	100	750	24
Y (HT)	100	1000	48
Er	100	800	24
Tm	100	800	24
Yb	100	500	24
Lu	100	850	24
compound	rate $[{\rm K}{\rm h}^{-1}]$	$T \ [^{\circ}C]$	dwell [h]
${\rm Li}_{3.05}{\rm Gd}_{0.95}{\rm Cd}_{0.05}{\rm I}_6$	100	800	24
${\rm Li}_{3.1}{\rm Gd}_{0.9}{\rm Cd}_{0.1}{\rm I}_6$	100	800	24
$Li_{3.25}Gd_{0.75}Cd_{0.25}I_6$	100	700	24
$Li_{2.20}Gd_{0.36}Cd_{0.36}I_4$	100	800	24
Li_3YBr_6	100	100	48
$\mathrm{Li}_{3}\mathrm{YBr}_{3.5}\mathrm{I}_{2.5}$	50	666	60
${\rm Li}_{3.1}{\rm Y}_{0.9}{\rm Cd}_{0.1}{\rm Br}_{3.5}{\rm I}_{2.5}$	50	666	60
${ m Li}_{3.1}{ m Y}_{0.9}{ m Ca}_{0.1}{ m Br}_{3.5}{ m I}_{2.5}$	50	666	60
$Li_{2.9}Y_{0.9}Zr_{0.1}Br_{3.5}I_{2.5}$	50	666	60

Table S1. Overview of the synthesis conditions of the respective Li_3MI_6 and substituted species.

X-Ray Diffraction Analysis

The powder X-ray diffraction (PXRD)-patterns were collected on a STOE Stadi-P diffractometer in Debye-Scherrer geometry, using Ag- $K_{\alpha 1}$ or Mo- $K_{\alpha 1}$ radiation from a primary Ge(111)-Johanntype monochromator and a triple array of DECTRIS Mythen2 1K detectors. The samples were sealed in 0.3 mm diameter borosilicate glass capillaries (HILGENBERG glass No. 14), which were spun during the measurement. The TOPAS 6.0^3 software was used to analyze the PXRD patterns. The background of the diffraction patterns was modelled by Chebychev polynomials of 6^{th} order and the peak profile by using the fundamental parameter approach implemented into TOPAS $6.0.^{4,5}$ The instrumental resolution function had been determined by a LeBail fit⁶ of a LaB₆ standard measurement prior to the experiments. The layer constitution was derived from our previous investigation on $Li_3HoBr_{6-x}I_x$.² For the refinement a recursive supercell approach implemented into TOPAS^{7,8} was used to average the calculated PXRD patterns of randomly created stacks of layers. Therefore, the monoclinic unit cell was transformed into a pseudo-orthorhombic unit cell with space group P1 according to a procedure published elsewhere.^{9,10} From the layer constitution, we derived possible stacking vectors and a faulting scenario as described in our previous works.^{9–12} The creation of the stacking sequences was directed by transition probabilities, *i.e.* fault probabilities that were optimized using grid search algorithms.^{10,11} For each refinement the diffraction patterns of 100 stacks consisting of 200 layers were averaged. For the final Rietveld refinements, constraints¹⁰ were applied on the atomic positions in order to maintain the intra-layer symmetry. The domain sizes were estimated from the full width at half maximum (FWHM) of distinct reflections. To this end, single peaks were fitted using a Lorentzian function and the instrumental broadening, which was determined from a deconvolution of a LaB_6 standard measurement.

In the diffraction patterns of the ball-milled samples given in Fig. S4a all reflections between 4.75 and 8.25° indicating a monoclinic space group symmetry and therefore partial ordering of the intra-layer cations² are absent. The patterns resemble diffraction data of CdCl₂-type materials and can indeed be indexed with a comparatively small rhombohedral unit cell with a = 4.29 Å and c = 21.04 Å for Li₃TmI₆. We also obtained a good fit of the powder pattern (see Fig. S1) with acceptable quality criteria ($R_{wp} = 2.97\%$, G.O.F. = 2.4) using the small rhombohedral unit cell with a staggered arrangement of (Li_{0.67}Tm_{0.33})I_{6/3}^{0.33}-layers, *i.e.* full intra-layer cation disorder and partially occupied inter-layer voids, (Li_{0.33} $\Box_{0.66}$)^{0.33+}, for a fully weighted Rietveld¹³ refinement. When using a rhombohedral cell and a completely disordered

intra-layer cation sub-structure, all possible stacking vectors leading to octahedral inter-layer voids become symmetry-equivalent and hence diffraction effects caused by stacking fault disorder do not need to be included in the refinements. It has to be noted that the local lattice symmetry of the ball-milled crystallites can be lower, but PXRD as a bulk method is based on strongly averaged diffraction data and therefore only yields averaged structure models.



Figure S1. Rietveld refinement of Li_3YI_6 after four steps of ball-milling and using a small rhombohedral unit cell with a full occupational disorder of intra-layer lithium and yttrium and leading to a R_p , R_{wp} and R_{Bragg} of 2.32, 2.97 and 1.34 %, respectively.

Table S2. Results of the Rietveld refinements of the differently synthesized Li_3MI_6 .

compound	$\stackrel{a}{[\text{Å}]}$	b [Å]	d_{001} [Å]	V [Å ³]	$M \\ [g \mathrm{mol}^{-1}]$	$\rho \\ [\rm gcm^{-3}]$	$\operatorname{SOF}(M)$	cd [%]	sfd [%]	R_{wp}
Li_3SmI_6	7.4863	12.9981	7.0455	685.58	932.60	4.518	0.71	44	100	7.54
Li ₃ GdI ₆	7.4562	12.9351	7.0205	677.10	939.49	4.608	0.65	53	100	7.76
Li ₃ TbI ₆	7.4675	12.9268	7.0215	677.79	941.17	4.612	0.68	49	100	7.50
Li ₃ DyI ₆	7.4296	12.8820	7.0175	671.63	944.74	4.672	0.75	38	100	8.99
Li ₃ HoI ₆	7.4370	12.8470	7.0000	668.80	947.17	4.703	0.61	59	100	8.00
Li_3YI_6 (LT)	7.4369	12.8719	7.0045	670.52	871.15	4.315	0.59	62	100	3.70
$Li_3YI_6^a$	4.2949	= a	21.0371	336.07	871.15	4.305	0.33	100	100	3.20
Li ₃ YI ₆ ^b	7.4350	12.8778	7.0045	670.66	871.15	4.314	0.77	35	0	2.57
Li_3YI_6 (HT)	7.4276	12.8955	7.0045	670.91	871.15	4.312	0.33	100	100	3.48
Li ₃ ErI ₆	7.4188	12.8386	7.0005	666.78	949.50	4.729	0.71	43	100	8.12
Li_3TmI_6	7.4188	12.8386	7.0005	666.78	951.18	4.738	0.63	55	100	7.08
$Li_3TmI_6^a$	4.2808	= a	20.9689	332.78	951.18	4.746	0.33	100	100	3.73
Li ₃ TmI ₆ ^b	7.4055	12.8253	7.0045	665.27	951.18	4.748	0.60	60	0	7.83
Li ₃ YbI ₆	7.4141	12.9103	7.0045	670.46	955.29	4.732	0.56	66	0	7.71
Li_3LuI_6	7.4149	12.7995	6.9705	661.55	957.21	4.805	0.46	82	100	7.76

cd = cation disorder within the intra-layer sfd = stacking fault disorder SOF = site occupation factor ^a obtained from BM and modelled with a trigonal cell ^b obtained from BM with subsequent annealing

The powder pattern of $\text{Li}_{1.5+5x}\text{Cd}_{0.50-x}\text{Gd}_{0.50-x}\text{I}_4$ with x = 0.14 was indexed by an iterative use of singular value decomposition (LSI).¹⁶ The process led to a *C*-centred unit cell with *C*2,



Figure S2. Rietveld refinement of Li_3YI_6 after mechanochemical ball-milling and subsequent annealing and leading to a R_p , R_{wp} and R_{Bragg} of 3.64, 5.73 and 1.57 %, respectively.



Figure S3. Rietveld refinement of Li_3YI_6 after conventional solid state synthesis leading to a R_p , R_{wp} and R_{Bragg} of 2.68, 3.48 and 1.35%, respectively.

Cm and C2/m as most probable space groups derived from the observed systematic reflection absences. The lattice parameters are given in Tab. S3. The background and the peak profile was modelled as described above. The crystal structure was solved by applying the global optimization method of simulated annealing (SA) in real space as it is implemented in TOPAS.¹⁷ During the process of crystal structure determination cadmium, gadolinium and iodide ions were



Figure S4. Comparison of the PXRD data for Li_3YI_6 and Li_3TmI_6 synthesized *via* different routes: (a) Selected reflections indicating a small, rhombohedral unit cell² with full occupational disorder of intra-layer lithium and thulium or yttrium, respectively. The domain size related broadening calculated from the FWHM for the 003 and 104 reflections are given, as well. (b) Comparison of microstructural parameters like vertical ([001] zones depicted as filled bars) and approximated lateral ([104] zones depicted as empty bars) domain size and intra-layer cation disorder .



Figure S5. Lattice parameters of the different Li_3MI_6 with M = Y, Sm, Gd–Lu as a function of the ionic radii of M.

moved freely throughout the unit cell. Atoms occupying special identical or special positions were identified by applying a merging radius of 0.7 Å.¹⁸ The iodide ions were quickly localized forming a cubic close packing (*ccp*) packed substructure with octahedral voids. Cadmium and



Figure S6. Melting points of $MI3^{14,15}$ (SmI₂ for samarium) and synthesis temperature of (a) Li₃YI₆ obtained from HT and LT solid-state synthesis and of (b) Li₃ MI_6 with M = Y, Sm, Gd–Lu with intra-layer cation disorder and stacking fault disorder as a function of the ionic radii of M.

gadolinium were found to partially occupy an identical 2b site. Small amounts of residual electron density indicating occupation by lithium were found in all octahedral voids by inspection of the difference Fourier map. Hence all available sites were populated by lithium and the 2bsite partially occupied by cadmium and gadolinium with a accumulated occupancy below one was filled with lithium cations. The total occupation of lithium and the heavy metals was constrained to the amount of iodide anions in the unit cell, in order to maintain charge balance. The final agreement factors are listed in Tab. S3, the atomic coordinates are given in Tab. S4. The fit of the whole powder pattern is shown in the † Electronic Supplementary Information (ESI) in Fig. S7. The crystallographic data have been deposited at Cambridge Crystallographic Data Centre (CCDC), deposit number: 2222205 For the Rietveld refinement of the cadmium substituted lithium gadolinium iodides inclusion of the $Li_{1.5+5x}Cd_{0.50-x}Gd_{0.50-x}I_4$ was necessary due to the presence of the 020 and 001 reflections of the latter phase. As no splitting of the $Li_{3+y}Gd_{1-y}Cd_yI_6$ related 001 reflection was observed, we constrained the lattice parameters of the two phases (see Tab. S5) in order to simulate crystallographic intergrowth and to minimize the parameter space. For further stabilization of the refinement, we also constrained the Cd/Gd occupancies of both phases and fixed it to the Cd/Gd ratio applied in the synthesis.



Figure S7. Rietveld refinement of $Li_{1.5+5x}Cd_{0.5-x}Gd_{0.5-x}I_4$ with x = 0.14.



Figure S8. PXRD pattern of the obtained product for the synthesis targeting $Li_{3.75}Cd_{0.75}Gd_{0.25}I_6$, reflection positions of possible impurities are highlighted. Due to the identical iodide substructures of the main phase and LiI, the latter cannot be distinguished, but most likely occurrs as an impurity.

chemical formula	$Li_{2.2}Cd_{0.36}Gd_{0.36}I_4$
molecular formula	$Li_{1.5+5x}Cd_{0.50-x}Gd_{0.50-x}I_4$
temperature [°C]	25
λ [Å]	0.55941
space group	$C2/m \ (\# \ 12)$
a [Å]	8.5621(9)
b [Å]	12.1258(15)
c [Å]	4.2867(5)
β [°]	90.115 (7)
$V [\text{\AA}^3]$	445.05 (9)
$\rho_{calc} \ [\mathrm{gcm^{-3}}]$	4.63
$R_p \left[\%\right]^*$	4.79
R_{wp} $[\%]^*$	5.43
$R_{Bragg} \left[\%\right]^*$	2.38
2θ range [°]	3.9-58.0
step width [°]	0.015
scan time [h]	4
no. of variables	38

Table S3. Crystallographic and Rietveld refinement data of $\text{Li}_{1.5+5x}\text{Cd}_{0.5-x}\text{Gd}_{0.5-x}\text{I}_4$ with x = 0.14 at room temperature.

* R_p , R_{wp} and R_{Bragg} as defined in TOPAS 6.0¹⁹

Table S4. Fractional coordinates of $\text{Li}_{1.5+5x}\text{Cd}_{0.5-x}\text{Gd}_{0.5-x}\text{I}_4$ with x = 0.14 at room temperature.

atom	Wyckoff	site	x	y	z	SOF	$B_{iso} [\text{\AA}^2]$
Cd1	2b	2/m	0.5	0	0	0.356(2)	2.9(1)
$\mathrm{Gd1}$	2b		0.5	0	0	0.356(2)	2.9(1)
Li1	2b		0.5	0	0	0.288(2)	2.9(1)
Li2	2a	2/m	0.5	0.5	0	0.91(7)	4.0(1)
Li3	4f	-1	0.75	0.75	0.5	0.51(7)	4.0(1)
I1	4g	2	0	0.2572(2)	0	1	1.7(1)
I2	4i	M	0.2545(5)	0.5	0.492(3)	1	$1.7\left(1 ight)$

Table S5. Constraints on the lattice parameters of Li_3GdI_6 and $\text{Li}_{1.5+5x}\text{Cd}_{0.5-x}\text{Gd}_{0.5-x}\text{I}_4$ used for the two phase refinements of cadmium substituted lithium gadolinium iodides.

${\rm Li}_3{\rm GdI}_6$	$\mathrm{Li}_{1.5+5x}\mathrm{Cd}_{0.50-x}\mathrm{Gd}_{0.50-x}\mathrm{I}_4$	constraint
a'	a	$a = \sqrt{3 \left[d \left(001\right)\right]^2 - \frac{4}{3} \frac{a'^2}{a'^2}}$
b'	b	$b = \sqrt{\frac{16}{3} a'^2 - 3 \left[d \left(001 \right) \right]^2}$
c'	c	$c = \frac{1}{3}b'$
eta^{\prime}	eta	eta

Table S6. Results of the Rietveld refinements of the different cadmium substituted lithium gadolinium iodides $Li_{3+x}Gd_{1-x}Cd_xI_6$.

x	a [Å]	b [Å]	d_{001} [Å]	V [Å ³]	$M \\ [g mol^{-1}]$	$_{[\rm gcm^{-3}]}^{\rho}$	$\operatorname{SOF}(M)$	cd [%]	sfd [%]	R_{wp}
0.05	7.4650	12.9177	7.0193	676.88	937.60	4.600	0.76	36	100	3.88
0.10	7.4472	12.9338	7.0192	676.09	935.70	4.596	0.75	38	100	4.95
0.25	7.4574	12.8977	6.9860	671.94	930.02	4.597	0.44	84	100	6.20

 $\rm cd=cation$ disorder within the intra-layer $~~\rm sfd=stacking~fault$ disorder $~~\rm SOF=site~occupation~factor$



Figure S9. Results of the PXRD patterns of the anion substituted Li₃YBr_{3.5}I_{2.5} and of the additionally cation substituted Li_{3.1}Y_{0.9}Cd_{0.1}Br_{3.5}I_{2.5}, Li_{3.1}Y_{0.9}Ca_{0.1}Br_{3.5}I_{2.5} and Li_{2.9}Y_{0.9}Zr_{0.1}Br_{3.5}I_{2.5}. (a) Rietveld refinements and (b) unit cell volumes as a function of the mean bond distance and of the ionic radii of the substituent. Here, the mean bond distances of the binary bromides and iodides are compared with the values obtained from Rietveld refinements of the mixed substituted Li_{3±y}Y_{1-y} $M_y^{II/IV}$ Br_{3.5}I_{2.5}.

Table S7. Results of the Rietveld refinements of the different pure and substituted lithium yttrium halides.

compound	a [Å]	b [Å]	d_{001} [Å]	V [Å ³]	M $[g mol^{-1}]$	$_{[\rm gcm^{-3}]}^{\rho}$	$\operatorname{SOF}(M)$	cd [%]	sfd [%]	R_{wp}
$\begin{array}{c} Li_3YBr_6\\ Li_3YBr_{3.5}I_{2.5}\\ Li_{3.1}Y_{0.9}Cd_{0.1}Br_{3.5}I_{2.5}\\ Li_{3.1}Y_{0.9}Ca_{0.1}Br_{3.5}I_{2.5}\\ Li_{2.9}Y_{0.9}Zr_{0.1}Br_{3.5}I_{2.5} \end{array}$	$\begin{array}{c} 6.9097 \\ 7.1531 \\ 7.1425 \\ 7.1697 \\ 7.1513 \end{array}$	11.9706 12.3812 12.3420 12.3811 12.3383	$\begin{array}{c} 6.4483 \\ 6.7383 \\ 6.7316 \\ 6.7514 \\ 6.7350 \end{array}$	533.36 596.77 593.41 599.31 594.26	589.15 706.65 709.69 702.46 706.19	3.668 3.933 3.972 3.893 3.947	$\begin{array}{c} 0.91 \\ 0.65 \\ 0.51 \\ 0.33 \\ 0.53 \end{array}$	$14 \\ 53 \\ 74 \\ 100 \\ 71$	$100 \\ 100 \\ 100 \\ 100 \\ 100 \\ 100$	3.72 3.11 2.83 2.67 2.76

cd = cation disorder within the intra-layer sfd = stacking fault disorder SOF = site occupation factor

X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) data were acquired with a Kratos Axis Ultra using monochromated Al- $K_{\alpha 1}$ radiation (1486.6 eV). A pass energy of 20 eV was used for high-resolution spectra. A charge neutralizer was used and the C 1s binding energy was calibrated to 284.8 eV. The samples were pressed into pellets and mounted onto the sample holder with a double-sided tape. The samples were transferred from the glovebox to the XPS system in an airtight transfer tool using Ar as protective atmosphere.



Figure S10. X-ray photoelectron spectra of (a) the I 3d peaks, (b) the Tm 4d signals and (c) the valence band of TmI₃ and Li₃TmI₆.

Solid-State NMR

All ^{6,7}Li-solid state nuclear magnetic resonance (ssNMR) measurements were performed on a BRUKER Avance-III 400 MHz wide bore spectrometer in a magnetic field of 9.4 T and ⁸⁹Y-ssNMR on a BRUKER Neo 600 MHz wide bore spectrometer in a magnetic field of 14.1 T. ⁷Li (Larmor frequency 155.5 MHz), ⁶Li (Larmor frequency 58.9 MHz) and ⁸⁹Y (Larmor frequency 29.4 MHz) magic angle spinning (MAS) spectra were recorded in 4 mm ZrO₂ rotors using a BRUKER BL4 MAS probe at spinning speed of 10 kHz. Due to the high reactivity of the studied materials, they were flame sealed in pyrex MAS inserts for BRUKER 4 mm rotors (Wilmad Glass, product # DWGSK2576-1). The measurements were performed using a simple Bloch Decay excitation scheme with a total of 32 to 4096 accumulations in each experiment. The relaxation delays were set sufficiently long to provide for a complete relaxation of magnetization and ensure quantitative measurements. ⁶Li and ⁷Li spectra were referenced to the external signals of 1 M solution of LiCl. ⁸⁹Y was referenced absolutely to the signal of tetramethylsilane.²⁰



Figure S11. Comparison of the (a) ⁷Li- and (b) ⁶Li-ssNMR spectra of Li₃YI₆ obtained *via* mechanochemical MCBM without and with subsequently annealing as well as from HT-SSS, and of the (c) ⁸⁹Y-ssNMR spectra of Li₃YBr₆ and Li₃YI₆ obtained *via* HT-SSS and of Li₃YI₆ from mechanochemical MCBM with subsequently annealing.

⁶ Li	$\delta~[\rm ppm]$	FWHM [ppm]	area $[\%]$
BM $\#3$	-3.48	0.57	54
	-3.09	1.43	46
BM $\#4$	-3.47	0.29	36
	-3.18	0.73	64
annealed	-3.74	0.35	38
	-3.43	0.74	62
SSS	-4.50	0.17	<1
	-3.94	0.14	31
	-3.71	0.32	69
⁷ Li	δ [ppm]	FWHM [ppm]	area [%]
⁷ Li BM #3	δ [ppm] -4.42	FWHM [ppm] 0.81	area [%] 4
⁷ Li BM #3	δ [ppm] -4.42 -3.34	FWHM [ppm] 0.81 1.08	area [%] 4 44
⁷ Li BM #3	δ [ppm] -4.42 -3.34 -2.87	FWHM [ppm] 0.81 1.08 4.10	area [%] 4 44 52
⁷ Li BM #3 BM #4	δ [ppm] -4.42 -3.34 -2.87 -3.43	FWHM [ppm] 0.81 1.08 4.10 0.42	area [%] 4 44 52 37
⁷ Li BM #3 BM #4	δ [ppm] -4.42 -3.34 -2.87 -3.43 -2.99	FWHM [ppm] 0.81 1.08 4.10 0.42 2.26	area [%] 4 44 52 37 63
⁷ Li BM #3 BM #4 annealed	$\begin{array}{c} \delta \ [\mathrm{ppm}] \\ -4.42 \\ -3.34 \\ -2.87 \\ -3.43 \\ -2.99 \\ -3.68 \end{array}$	FWHM [ppm] 0.81 1.08 4.10 0.42 2.26 0.43	area [%] 4 44 52 37 63 30
⁷ Li BM #3 BM #4 annealed	$\begin{array}{c} \delta \ [\mathrm{ppm}] \\ -4.42 \\ -3.34 \\ -2.87 \\ -3.43 \\ -2.99 \\ -3.68 \\ -3.37 \end{array}$	FWHM [ppm] 0.81 1.08 4.10 0.42 2.26 0.43 1.21	area [%] 4 44 52 37 63 30 70
⁷ Li BM #3 BM #4 annealed SSS	$\begin{array}{c} \delta \ [\mathrm{ppm}] \\ -4.42 \\ -3.34 \\ -2.87 \\ -3.43 \\ -2.99 \\ -3.68 \\ -3.37 \\ -3.96 \end{array}$	FWHM [ppm] 0.81 1.08 4.10 0.42 2.26 0.43 1.21 0.22	area [%] 4 44 52 37 63 30 70 31

Table S8. Deconvolution of the signals observed in 6 Li- and 7 Li-ssNMR for Li₃YI₆ after ball milling, annealing and conventional synthesis.



Figure S12. Comparison of the (a) ⁶Li- and (b) ⁷Li-ssNMR spectra of Li₃YBr₆, Li₃YI₆, Li₃YBr_{3.5}I_{2.5}, Li_{3.1}Y_{0.9} $M^{II}_{0.1}$ Br_{3.5}I_{2.5} with $M^{II} =$ Cd, Ca and Li_{2.9}Y_{0.9}Zr_{0.1}Br_{3.5}I_{2.5}. The asterisk corresponds to signal originating from an impurity of LiI.

⁶ Li	δ [ppm]	area [%]	FWHM [ppm]
Li ₃ YBr ₆	-1.21	24	0.09
	-1.13	35	0.23
	-0.88	41	0.64
Li_3YI_6	-3.71	69	0.32
	-3.94	31	0.14
	-4.50	<1	0.17
$\mathrm{Li}_{3}\mathrm{YBr}_{3.5}\mathrm{I}_{2.5}$	-1.92	52	0.13
	-1.77	48	0.45
$Li_{3.1}Y_{0.9}Cd_{0.1}Br_{3.5}I_{2.5}$	-2.46	17	0.26
	-1.89	32	0.11
	-1.89	51	0.63
${\rm Li}_{3.1}{\rm Y}_{0.9}{\rm Ca}_{0.1}{\rm Br}_{3.5}{\rm I}_{2.5}$	-1.94	41	0.16
	-2.23	15	0.26
	-1.75	44	0.64
${ m Li}_{2.9}{ m Y}_{0.9}{ m Zr}_{0.1}{ m Br}_{3.5}{ m I}_{2.5}$	-1.80	16	0.13
	-1.57	66	0.36
	-1.21	18	0.85
⁷ Li	$\delta~[\rm ppm]$	area $[\%]$	FWHM [ppm]
Li_3YBr_6	-1.19	53	0.23
	-0.97	47	0.60
Li_3YI_6	-3.96	18	0.20
	-3.77	82	0.58
$\mathrm{Li}_{3}\mathrm{YBr}_{3.5}\mathrm{I}_{2.5}$	-1.93	34	0.17
	-1.82	66	0.66
${ m Li}_{3.1}{ m Y}_{0.9}{ m Cd}_{0.1}{ m Br}_{3.5}{ m I}_{2.5}$	-1.89	33	0.21
	-2.48	16	0.33
	-1.83	51	0.77
${ m Li}_{3.1}{ m Y}_{0.9}{ m Ca}_{0.1}{ m Br}_{3.5}{ m I}_{2.5}$	-1.94	29	0.23
	-2.28	13	0.32
	-1.78	58	0.83
${ m Li}_{2.9}{ m Y}_{0.9}{ m Zr}_{0.1}{ m Br}_{3.5}{ m I}_{2.5}$	-1.81	15	0.19
	-1.60	60	0.44
	-1.23	25	1.08

Table S9. Deconvolution of the signals observed in $^6\mathrm{Li-}$ and $^7\mathrm{Li-ssNMR}$ for different pure and substituted lithium yttrium halides.

Electrochemical Impedance Spectroscopy

For the electrochemical impedance spectroscopy (EIS) measurements 70 to 220 mg of ground samples were uniaxially pressed into pellets with a diameter of 5 mm, using a pressure of around 1 GPa, thus leading to thicknesses between 0.5 to 2.5 mm with relative densities of around 95% (see Fig. S13). In order to reduce the contact resistance the pellets were also coated with ruthenium or platinum films of around 200 nm with the use of a sputter coater (QUORUM Q150GB). The pellets were then contacted with stainless steel electrodes in an electrochemical cell (TSC Battery, RHD INSTRUMENTS). With the use of a spring with a spring constant of 32.6 N mm^{-1} pressures of around 10 MPa were applied during the measurements. An alternating current with an amplitude of 85 to 100 mV in a frequency range of 10^6 to 1 Hz were applied using an IVIUM compactstat.h or a NEISYS NOVOCONTROL potentiostat. The samples were cycled between -10 to $25 \,^{\circ}$ C in steps of $5 \,^{\circ}$ C. In order to get proper statistics two to four pellets of each sample with different thicknesses were measured.

The Nyquist and Bode plots (all at 25 °C) obtained from EIS for Li_3MI_6 with M = Y, Sm, Gd-Lu are depicted in Figs. S17-S26 with the respective equivalent circuit models (ECMs) used for fitting the data. Here, all compounds (except with M = Sm, Er, Yb and Lu) show two distinguishable semicircles followed by a polarization tail. Both semicircles were modelled with an ECM consisting of a resistor and constant phase element (CPE) in parallel. For the polarization tail another CPE was used for fitting. According to the setup, an inductor had to be included into the ECM for some samples. Samples measured with a different setup did not need an inductor to be included into the ECM. For M = Sm, Er and Lu the semicircle at lower frequencies could not be resolved properly and thus a reduced ECM consisting of an inductor, a parallel resistor and CPE and another CPE, all in series, was used for fitting. For Li_3YbI_6 an additional semicircle needed to be included and for the first semicircle a capacitor instead of a CPE was used for fitting. The values of the respective equivalent circuit elements (ECEs) are summarized in Tab. S10. The Nyquist and Bode plots for the Cd²⁺ substitution in $Li_{3+y}Gd_{1-y}Cd_yI_6$ and $Li_{2.20}Gd_{0.36}Cd_{0.36}I_4$ are given in Figs. S28–S31. The data for Li₃YBr₆, Li₃YBr_{3.5}I_{2.5}, Li_{3.1}Y_{0.9}Cd_{0.1}Br_{3.5}I_{2.5}, Li_{3.1}Y_{0.9}Ca_{0.1}Br_{3.5}I_{2.5} and Li_{2.9}Y_{0.9}Zr_{0.1}Br_{3.5}I_{2.5} are depicted in Figs. S32–S36, respectively. The EIS data obtained for the different synthetic approaches are given in Fig. S22 (SSS) and in Figs. S14 and S15 (mechanochemical MCBM and subsequent annealing). The total ionic conductivities were extracted from the ionic resistances of the semicircles contributing to bulk and grain boundary related process according to their

capacities²¹ between 10^{-12} to 10^{-11} F. Inactive data points were not included into the fitting.



Figure S13. Relative densities of the prepared pellets for EIS measurements of the different ${\rm Li}_3 M {\rm I}_6.$



Figure S14. Nyquist and Bode plots at 25° C of Li₃YI₆ obtained through mechanochemical milling: (a)–(c) after the last milling iteration and (d)–(f) after annealing.



Figure S15. Nyquist and Bode plots at 25°C of Li_3TmI_6 obtained through mechanochemical milling: (a)–(c) after the last milling iteration and (d)–(f) after annealing.



Figure S16. Arrhenius plots of the ionic conductivity for the different lithium rare earth halides. (a) Li_3MI_6 with M = Y, Sm, Gd–Lu, (b) $\text{Li}_{3+y}\text{Gd}_{1-y}\text{Cd}_y\text{I}_6$, (c) different bare and substituted lithium yttrium halides and (d) Li_3YI_6 and Li_3TmI_6 obtained *via* different synthetic routes.



Figure S17. Impedance spectra of Li_3SmI_6 at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S18. Impedance spectra of $\rm Li_3GdI_6$ at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S19. Impedance spectra of Li_3TbI_6 at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S20. Impedance spectra of Li_3DyI_6 at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S21. Impedance spectra of Li_3HoI_6 at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S22. Impedance spectra at 25°C in Nyquist and Bode representation of Li_3YI_6 obtained *via* low and high temperature solid state synthesis in (a)–(c) and (d)–(f), respectively.



Figure S23. Impedance spectra of Li_3ErI_6 at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S24. Impedance spectra of $\rm Li_3TmI_6$ at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S25. Impedance spectra of Li_3YbI_6 at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S26. Impedance spectra of $\rm Li_3LuI_6$ at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S27. Meyer-Neldel plot of (a) the pre-exponential factor σ_0 or of (b) the ionic conductivity σ against the activation energy for ion diffusion for different synthesized halides.

M	$d \ [mm]$	$R_1 \ [\Omega]$	Q_1 [C]	α_1	$C_{Brug,1}$ [F]
Y (LT)	1.613	3.46×10^3	2.99×10^{-10}	0.81	1.24×10^{-11}
Y (HT)	1.666	5.69×10^{3}	2.40×10^{-10}	0.80	8.51×10^{-12}
Sm	1.837	1.47×10^3	2.93×10^{-10}	0.84	1.66×10^{-11}
Gd	2.121	2.24×10^3	7.81×10^{-11}	0.96	4.43×10^{-11}
Tb	1.390	3.20×10^3	4.53×10^{-10}	0.79	1.17×10^{-11}
Dy	1.337	4.18×10^3	1.76×10^{-10}	0.83	9.55×10^{-12}
Ho	1.837	4.42×10^3	1.28×10^{-10}	0.86	1.31×10^{-11}
\mathbf{Er}	2.136	1.21×10^4	8.58×10^{-11}	0.87	1.17×10^{-11}
Tm	1.920	3.18×10^3	7.38×10^{-11}	0.96	3.83×10^{-11}
Yb	1.549	4.30×10^3	—	—	1.06×10^{-11}
		—	4.37×10^{-10}	0.89	8.33×10^{-11}
Lu	1.319	2.12×10^4	1.45×10^{-10}	0.83	1.14×10^{-11}
M		$R_2 \ [\Omega]$	Q_2 [C]	α_2	$C_{Brug,2}$ [F]
Y(LT)		6.03×10^{2}	1.00×10^{-5}	0.55	1.53×10^{-7}
Y (HT)		1.75×10^3	1.51×10^{-5}	0.57	9.72×10^{-7}
Sm		_	6.73×10^{-5}	0.56	_
Gd		3.21×10^3	1.71×10^{-5}	0.73	5.91×10^{-6}
Tb		1.13×10^3	5.29×10^{-5}	0.40	7.72×10^{-7}
Dy		1.37×10^2	3.17×10^{-5}	0.60	8.38×10^{-7}
Ho		6.02×10^2	1.60×10^{-5}	0.50	1.62×10^{-7}
\mathbf{Er}		_	1.73×10^{-5}	0.68	_
Tm		4.54×10^3	2.84×10^{-5}	0.33	4.15×10^{-7}
Yb		3.75×10^3	2.31×10^{-6}	0.43	8.33×10^{-11}
Lu		-	3.68×10^{-5}	0.41	
М		$R_3 \ [\Omega]$	$Q_3[C]$	α_3	Ι
Y(LT)		_	3.03×10^{-5}	0.83	6.42×10^{-5}
Y (HT)		_	2.54×10^{-6}	0.83	_
Sm		_	_	_	3.56×10^{-5}
Gd		_	1.99×10^{-5}	0.89	1.82×10^{-4}
Tb		_	7.27×10^{-6}	0.82	6.73×10^{-5}
Dy		_	3.65×10^{-5}	0.81	4.93×10^{-5}
Ho		_	3.06×10^{-5}	0.83	9.51×10^{-5}
\mathbf{Er}		_	_	_	4.50×10^{-4}
Tm		_	2.7×10^{-4}	0.89	2.20×10^{-4}
Yb		3.58×10^3	9.80×10^{-4}	0.28	_
Lu		_	_	_	2.39×10^{-4}

Table S10. Values of the respective equivalent circuit elements (ECEs) of the equivalent circuit models used for the different Li_3MI_6 compounds with M = Y, Sm, Gd–Lu, all at 25°C.



Figure S28. Impedance spectra of the product of the synthesis of $\text{Li}_{3+y}\text{Gd}_{1-y}\text{Cd}_y\text{I}_6$ with y = 0.05 at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S29. Impedance spectra of the product of the synthesis of $\text{Li}_{3+y}\text{Gd}_{1-y}\text{Cd}_y\text{I}_6$ with y = 0.10 at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S30. Impedance spectra of the product of the synthesis of $\text{Li}_{3+y}\text{Gd}_{1-y}\text{Cd}_y\text{I}_6$ with y = 0.25 at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S31. Impedance spectra of the product of the synthesis of $Li_{2.20}Gd_{0.36}Cd_{0.36}I_4$ at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S32. Impedance spectra of $\rm Li_3YBr_6$ at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S33. Impedance spectra of $\rm Li_3YBr_{3.5}I_{2.5}$ at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S34. Impedance spectra of $Li_{3.1}Y_{0.9}Cd_{0.1}Br_{3.5}I_{2.5}$ at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S35. Impedance spectra of $Li_{3.1}Y_{0.9}Ca_{0.1}Br_{3.5}I_{2.5}$ at 25°C in (a) Nyquist and (b) and (c) Bode representation.



Figure S36. Impedance spectra of $Li_{2.9}Y_{0.9}Zr_{0.1}Br_{3.5}I_{2.5}$ at 25°C in (a) Nyquist and (b) and (c) Bode representation.

Bond Valence Sum Calculations



Figure S37. bond valence energy landscape (BVEL) of $Li_{2.2}Gd_{0.36}Cd_{0.36}I_4$ obtained from bond valence sum (BVS) calculations within (a) the mixed chain-like layer in the (110)-plane, (b) the solely lithium containing honeycomb inter-layer in the (110)-plane and (c) between the stacked layers in the *ab*-plane. Only the coordination polyhedra of mixed occupied 2*b* sites are depicted.

Pulsed-Field-Gradient NMR

⁷Li pulsed-field-gradient nuclear magnetic resonance (PFG-NMR) diffusion measurements were conducted on a BRUKER Avance III 400 MHz instrument equipped with a diff60 gradient probe (max. gradient of $2900 \,\mathrm{G \, cm^{-1}}$). Data were acquired using a stimulated echo sequence with diffusion times in the range of 25 to 100 ms and effective gradient durations of 1 to 3 ms. The measured echo-signal attenuation peaks were phase corrected, and the integrated areas were used to extract the diffusivities.

The determined tracer diffusion coefficients D_{tr}^{NMR} are connected to the uncorrelated diffusion coefficient D_{uc}^{NMR} according to eq. (1), using the Bardeen-Herring tracer correlation factor of $f = 1.^{22,23}$

$$D_{tr}^{\rm NMR} = f D_{uc}^{\rm NMR} \tag{1}$$

Thus, the mean diffusion lengths $\langle r \rangle$ can be estimated using the diffusion time Δ^{NMR} according to eq. (2).^{24,25}

$$\langle r \rangle = \sqrt{2D_{uc}^{\rm NMR} \Delta^{\rm NMR}} \tag{2}$$

The diffusion jump rate τ^{-1} was calculated from the length of a jump l (estimated from softBV calculations of perfectly ordered Li₃HoBr₆ and Li₃HoI₆ from Plass *et al.*² to range from 2.643 to 3.147 Å) and D_{tr}^{NMR} according to eq. (3) and assuming a 3D-diffusion mechanism.²³

$$\tau^{-1} = \frac{6D_{tr}^{\rm NMR}}{l^2 f} \tag{3}$$

The estimated mean diffusion lengths $\langle r \rangle$ and diffusion jump rates τ^{-1} are summarized in Fig. S39d. Here, Li₃YBr₆ shows a 50% greater mean diffusion length compared to Li₃YI₆ (786 nm vs. 478 nm). The same trend can be observed for the jump rates, which were estimated to 2.7×10^8 and $9.8 \times 10^7 \,\mathrm{s}^{-1}$ for lithium yttrium bromide $(7.3 \times 10^8 \,\mathrm{s}^{-1}$ for MCBM with subsequent annealing from Gombotz and Wilkening²⁶) and iodide, respectively. Judging by the observed increase in the $D_{tr}^{\rm NMR}$, the solely anion substituted Li₃YBr_{3.5}I_{2.5} as well as the additionally cation substituted Li_{2.9}Y_{0.9}Zr_{0.1}Br_{3.5}I_{2.5} exhibit increased mean diffusion lengths of 997 and 1102 nm and enhanced jump rates of 4.3×10^8 and $5.2 \times 10^8 \,\mathrm{s}^{-1}$, respectively. In comparison, the divalent substituted Li_{3.1}Y_{0.9} $M^{\rm H}_{0.1}$ Br_{3.5}I_{2.5} with $M^{\rm H} =$ Cd, Ca show slightly smaller values for the mean diffusion lengths of 833 and 777 nm as well as for the jump rates of $3.0 \times 10^8 \,\mathrm{and} 2.6 \times 10^8 \,\mathrm{s}^{-1}$, respectively. At 25 °C the spin-lattice relaxation times T_1 range

between 560 to 1300 ms and spin-spin relaxation times T_2 between 600 to 1400 ts (see Fig. S39a). The most likely reason for the demonstrated increase of spin-lattice relaxation rate is a higher mobility of Li ions.

Such a large variation in relaxation times clearly indicates changes in the mobility of the lithium ions. The jump rates increase from 1.1×10^8 to $3.6 \times 10^8 \,\mathrm{s}^{-1}$ and to $4.2 \times 10^8 \,\mathrm{s}^{-1}$ for the MCBM, subsquently annealed and SSS sample, respectively. The mean diffusion length increases from 496 nm to 917 nm and to 985 nm for the MCBM, subsquently annealed and SSS sample. Indeed, the vertical and lateral dimensions of the determined domain sizes (≈ 5 to $15 \,\mathrm{nm}$) are significantly smaller compared to the mean diffusion lengths observed during the PFG-NMR measurements, but unfortunately no conclusion about the underlying diffusion process (inter- or intra-crystalline) can be drawn. The SSS, MCBM and subsequently annealed samples exhibit prominent ranges of ⁷Li spin-lattice relaxation times T_1 of 599, 3430 and 1300 ms and spin-spin relaxation times T_2 of 1382, 429 and 508 ts (at $25 \,^{\circ}$ C), respectively. As mentioned above, the most likely reason for a decrease in spin-lattice relaxation times is a higher mobility of Li ions in the SSS compared to MCBM with or without subsequent annealing.

Table S11. Overview of disorder, purity and electrochemical properties of the different Li_3MI_6 with M = Y, Sm, Gd–Lu.

М	cation disorder [%]	stacking fault disorder [%]	purity [wt.%]	$ \begin{array}{c} \sigma^{\rm EIS}_{ion} \left(20^{\circ}{\rm C} \right) \\ [{\rm Scm^{-1}}] \end{array} $	$\begin{array}{c} E_a^{\rm EIS} \\ [eV] \end{array}$
Sm	44	100	100	4.6×10^{-4}	0.33
Gd	53	100	100	$3.9 imes 10^{-4}$	0.26
Tb	49	100	84	2.5×10^{-4}	0.23
Dy	38	100	100	1.8×10^{-4}	0.23
Но	59	100	100	1.7×10^{-4}	0.23
Y(LT)	62	100	94	1.9×10^{-4}	0.24
Y (HT)	100	100	90	$1.4 imes 10^{-4}$	0.23
Er	43	100	78	$1.0 imes 10^{-4}$	0.21
Tm	55	100	100	$2.8 imes 10^{-4}$	0.20
Yb	66	0	100	9.2×10^{-5}	0.26
Lu	82	100	100	3.0×10^{-5}	0.23



Figure S38. Relaxation times (T_1 and T_2) and PFG-NMR measurements for Li₃YI₆ obtained *via* SSS, mechanochemical MCBM and MCBM with subsequently annealing: (a) relaxation times, (b) Arrhenius plot of the tracer diffusion constant, (c) activation energy and tracer diffusion constant at a given temperature and (d) the obtained mean diffusion lengths and jump rates.

Table S12. Summary of the ionic transport properties obtained from EIS and PFG-NMR for the different substituted lithium yttrium halides.

compound	cation disorder [%]	$ \begin{array}{c} \sigma_{ion}^{\rm EIS} \left(20^{\circ}{\rm C} \right) \\ [{\rm Scm^{-1}}] \end{array} $	E_a^{EIS} [eV]	$D_{tr}^{\rm NMR} \left(25^{\circ}{\rm C} \right)$ [D]	$E_a^{\rm NMR}$ [eV]
Li ₃ YBr ₆	14	$1.7 imes 10^{-3}$	0.23	3.1×10^{-12}	0.31
Li ₃ YI ₆	100	1.4×10^{-4}	0.23	1.1×10^{-12}	0.33
$\mathrm{Li}_{3}\mathrm{YBr}_{3.5}\mathrm{I}_{2.5}$	53	2.8×10^{-3}	0.17	4.9×10^{-12}	0.28
$\rm Li_{3.1}Y_{0.9}Cd_{0.1}Br_{3.5}I_{2.5}$	74	1.7×10^{-3}	0.19	3.5×10^{-12}	0.28
${ m Li}_{3.1}{ m Y}_{0.9}{ m Ca}_{0.1}{ m Br}_{3.5}{ m I}_{2.5}$	100	1.8×10^{-3}	0.20	3.0×10^{-12}	0.31
${\rm Li}_{2.9}{\rm Y}_{0.9}{\rm Zr}_{0.1}{\rm Br}_{3.5}{\rm I}_{2.5}$	71	$3.0 imes 10^{-3}$	0.17	6.1×10^{-12}	0.28



Figure S39. Relaxation times (T_1 and T_2) and PFG-NMR measurements for different lithium yttrium halides: (a) relaxation times, (b) Arrhenius plot of the tracer diffusion constant, (c) activation energy and tracer diffusion constant at a given temperature and (d) the obtained mean diffusion lengths and jump rates.

References

- G. Meyer and L. R. Morss, Synthesis of Lanthanide and Actinide Compounds, Springer Netherlands, Dordrecht, 1991, vol. 2.
- (2) M. A. Plass, S. Bette, R. E. Dinnebier and B. V. Lotsch, Chem. Mater., 2022, 34, 3227–3235.
- (3) A. A. Coelho, J. Appl. Crystallogr., 2018, 51, 210–218.
- (4) R. Cheary, A. Coelho and J. Cline, J. Res. Natl. Inst. Stand. Technol., 2004, 109, 1.
- (5) R. W. Cheary and A. Coelho, J. Appl. Crystallogr., 1992, 25, 109–121.
- (6) A. Le Bail, H. Duroy and J. Fourquet, Mater. Res. Bull., 1988, 23, 447–452.
- (7) C. M. Ainsworth, J. W. Lewis, C.-H. Wang, A. A. Coelho, H. E. Johnston, H. E. A. Brand and J. S. O. Evans, *Chem. Mater.*, 2016, 28, 3184–3195.
- (8) A. A. Coelho, J. S. O. Evans and J. W. Lewis, J. Appl. Crystallogr., 2016, 49, 1740–1749.
- (9) S. Bette, T. Takayama, K. Kitagawa, R. Takano, H. Takagi and R. E. Dinnebier, *Dalton Trans.*, 2017, 46, 15216–15227.
- (10) S. Bette, T. Takayama, V. Duppel, A. Poulain, H. Takagi and R. E. Dinnebier, *Dalton Trans.*, 2019, 48, 9250–9259.
- (11) S. Bette, B. Hinrichsen, D. Pfister and R. E. Dinnebier, J. Appl. Crystallogr., 2020, 53, 76–87.
- (12) S. Bette and R. E. Dinnebier, Crystallography in Materials Science, De Gruyter, Berlin, Boston, 2021, ch. 2, pp. 55–92.
- (13) H. M. Rietveld, J. Appl. Crystallogr., 1969, 2, 65–71.
- (14) Taschenbuch f
 ür Chemiker und Physiker, ed. R. Blachnik, Springer Berlin Heidelberg, 4th edn, 1998.
- (15) CRC Handbook of Chemistry and Physics, ed. J. R. Rumble, CRC Press/Taylor & Francis, 103rd edn, 2022.
- (16) A. A. Coelho, J. Appl. Crystallogr., 2003, 36, 86–95.
- (17) A. A. Coelho, J. Appl. Crystallogr., 2000, **33**, 899–908.

- (18) V. Favre-Nicolin and R. erný, Mater. Sci. Forum, 2004, 443-444, 35-38.
- (19) A. A. Coelho, J. Appl. Crystallogr., 2018, 51, 210–218.
- (20) R. K. Harris, E. D. Becker, S. M. Cabral de Menezes, R. Goodfellow and P. Granger, Pure Appl. Chem., 2001, 73, 1795–1818.
- (21) J. T. S. Irvine, D. C. Sinclair and A. R. West, Adv. Mater., 1990, 2, 132–138.
- (22) J. Bardeen and C. Herring, in *Imperfections in Nearly Perfect Crystals*, ed. W. Shockley,
 J. H. Hollomon, R. Mauerer and F. Seitz, John Wiley & Sons, Inc., 1952, ch. Diffusion in Alloys and the Kirkendall Effect, pp. 261–288.
- (23) G. E. Murch, Solid State Ion, 1982, 7, 177–198.
- (24) M. A. Islam, *Phys. Scr.*, 2004, **70**, 120–125.
- (25) A. Kuhn, O. Gerbig, C. Zhu, F. Falkenberg, J. Maier and B. V. Lotsch, Phys. Chem. Chem. Phys., 2014, 16, 14669–14674.
- (26) M. Gombotz and H. M. R. Wilkening, ACS Sustain. Chem. Eng., 2021, 9, 743–755.