The cubic structure of Li_3As stabilized by pressure or configurational entropy via the solid solution Li_3As – Li_2Se

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Supporting information

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1. X-Ray powder diffraction

Index and refinement of the cubic polymorph β-Li_3As

Wavelength: 1.540598
Number of accepted peaks: 11
2Theta window: 0.050
2Theta zeropoint: -0.0354 (refineable)
Symmetry: Cubic F
Space group: $Fm\bar{3}m$ (No. 225)

Initial cell parameters:
Cell_A: 6.2148
Refined cell parameters:
Cell_A: 6.2148(12)
Cell_Volume: 240.04(8)

Number of single indexed lines: 11
Number of unindexed lines: 0
Profile Function: Pseudo-Voigt
2Theta zeropoint: -0.035(14)
Final 2Theta window: 0.0400

N	2Th[obs]	H	K	L	2Th[calc]	obs-calc	Int.	d[obs]	d[calc]
1	24.799	1	1	1	24.794	0.0051	100.0	3.5874	3.5881
2	28.707	2	0	0	28.706	0.0017	41.6	3.1072	3.1074
3	41.043	2	2	0	41.045	-0.0016	1.5	2.1973	2.1973
4	48.538	3	1	1	48.546	-0.0075	20.8	1.8741	1.8738
5	50.851	2	2	2	50.854	-0.0032	5.2	1.7942	1.7941
6	59.450	4	0	0	59.443	0.0070	2.6	1.5535	1.5537
7	65.399	3	3	1	65.404	-0.0045	5.3	1.4259	1.4258
8	67.314	4	2	0	67.325	-0.0118	3.6	1.3899	1.3897
9	74.811	4	2	2	74.776	0.0354	4.3	1.2681	1.2686
10	80.160	5	1	1	80.188	-0.0277	3.5	1.1964	1.1960
11	89.045	4	4	0	89.038	0.0071	1.0	1.0986	1.0986

Average delta(2Theta) = 0.010
Maximum delta(2Theta) = 0.035 (peak 9) = 3.5 * average
Figure of Merit F(11) = 89.6 (0.010, 12)
Durbin-Watson serial correlation = 3.325
Sqrt[sum(w * delta(q)^2) / (Nobs - Nvar)] = 0.0001267
Program: STOE-WinXPOW, Vol. Version 3.0.2.5, STOE & Cie GmbH Darmstadt, 2011.

The system Li_3As – Li_2Se

Table S1. Lattice parameters of $Li_{3-x}As_{1-x}Se_x$ (0.2 ≤ *x* ≤ 1).

x	*a* / Å
0.2	6.1573(2)
0.3	6.1614(4)
0.4	6.1404(2)
0.5	6.1126(2)
0.6	6.0770(2)
0.7	6.0445(2)
0.8	6.01576(14)
0.9	6.00524(19)

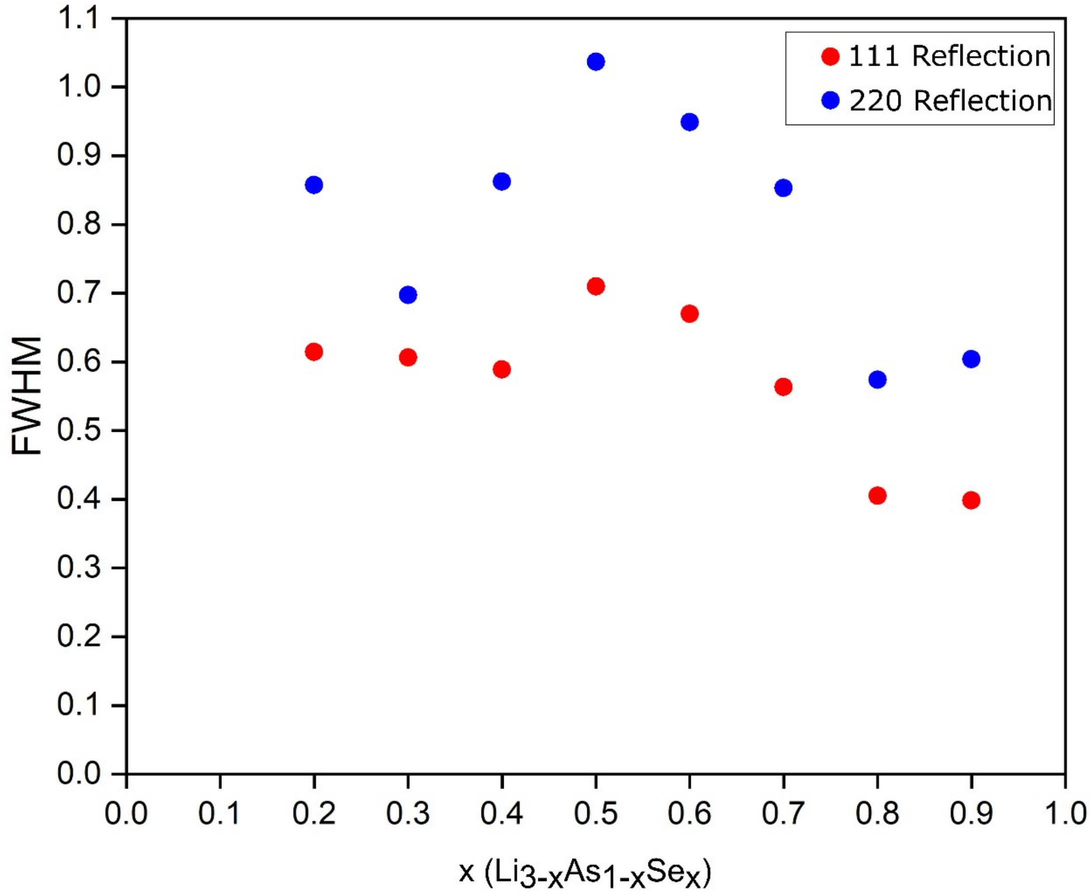


Figure S1. Diagram of the **F**ull **W**idth at **H**alf **M**aximum (**FWHM**) depending on the mole fraction *x* in the solid solution $Li_{3-x}As_{1-x}Se_x$ (0.2 ≤ *x* ≤ 1). The FWHM was determined for the first (111 Reflex, red) and third (220 Reflex, blue) reflection of the cubic reflexion profiles in Figure 4. For *x* = 0.2 - 0.6, 36 milling cycles were applied and for *x* = 0.7 – 0.9, 12 milling cycles were applied. Therefore, the crystallinity of the ball milled samples corresponds with the number of ball mill cycles.

2. Thermal analysis

The system Li_3As – Li_2Se

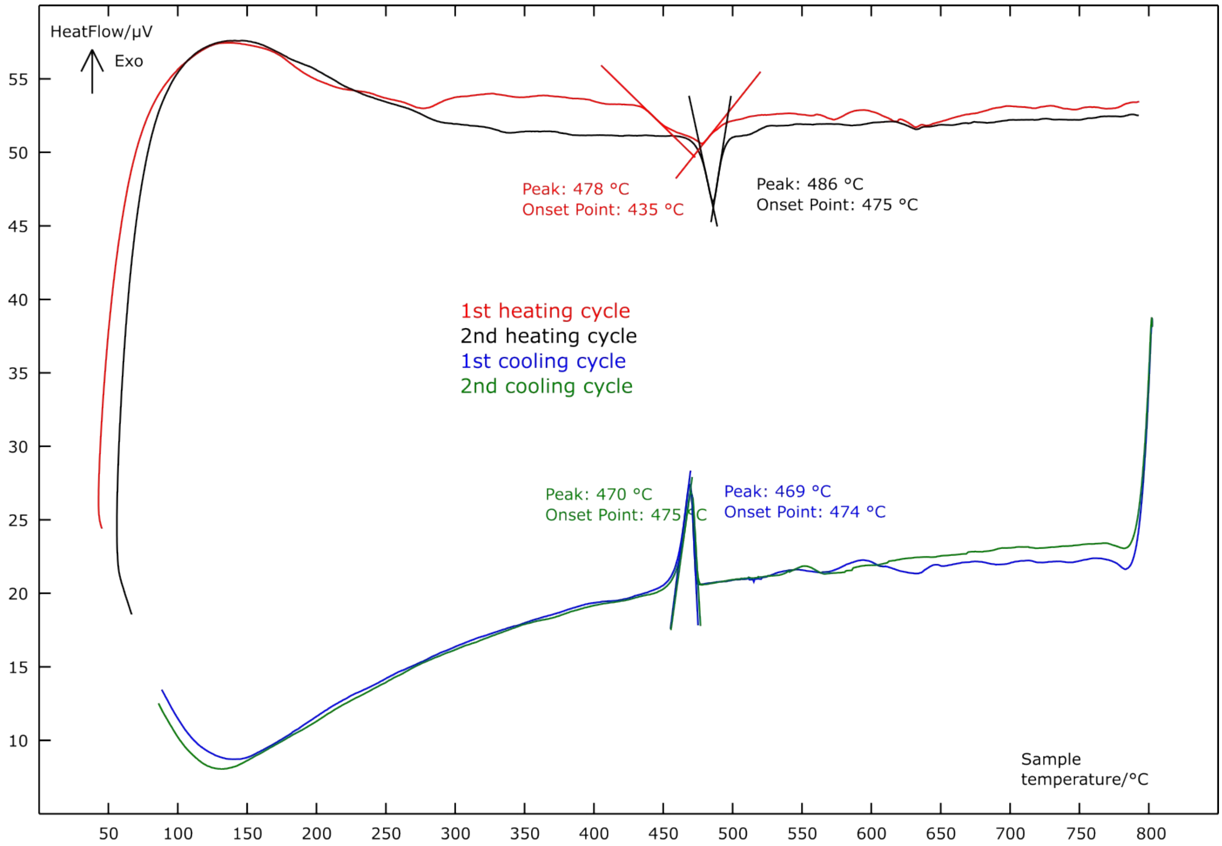


Figure S2. Differential thermal analysis of $Li_{2.6}As_{0.6}Se_{0.4}$ showing endothermal effects in the heating cycles (red and black) and exothermal effects in the cooling cycles (blue and green).

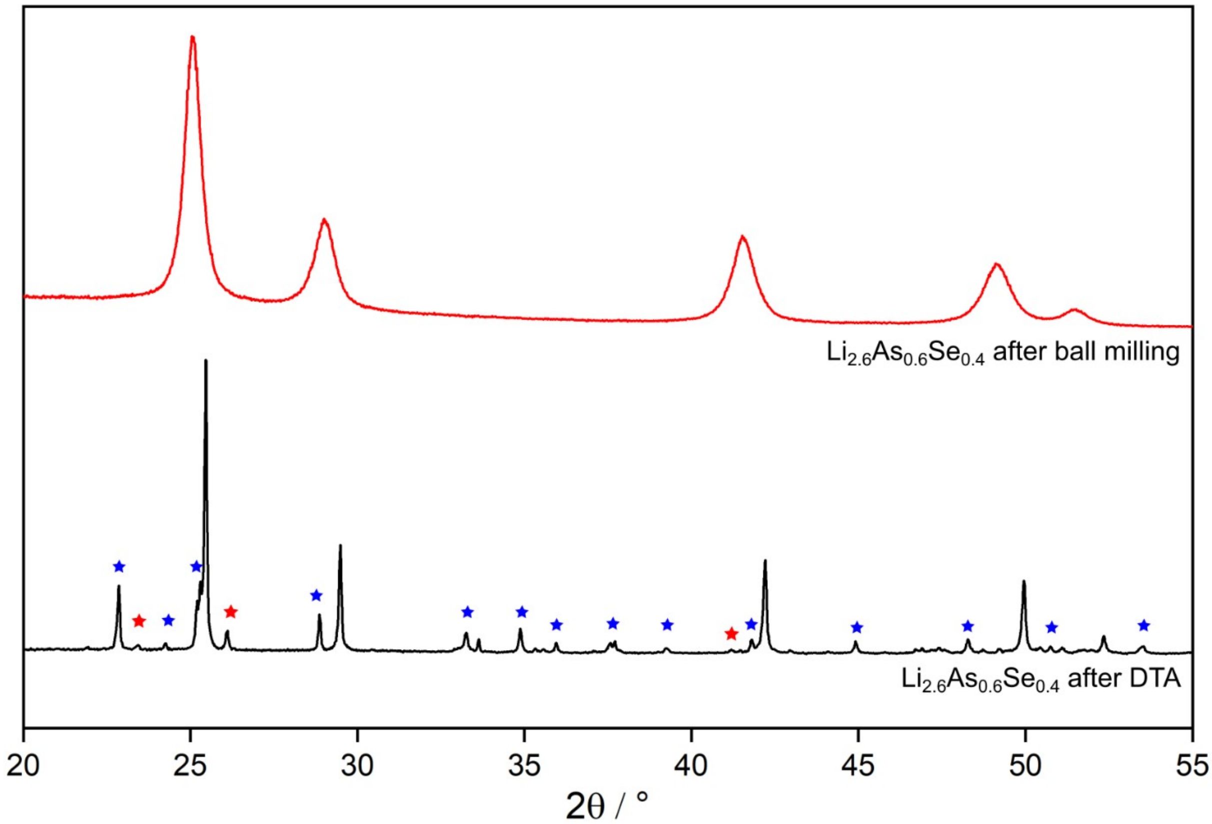


Figure S3. Powder diffractogram of $Li_{2.6}As_{0.6}Se_{0.4}$ after ball milling (red) and after DTA (black). Intensities marked with a red star can be assigned to Li_3As and intensities marked with a blue star can be assigned to LiAs.

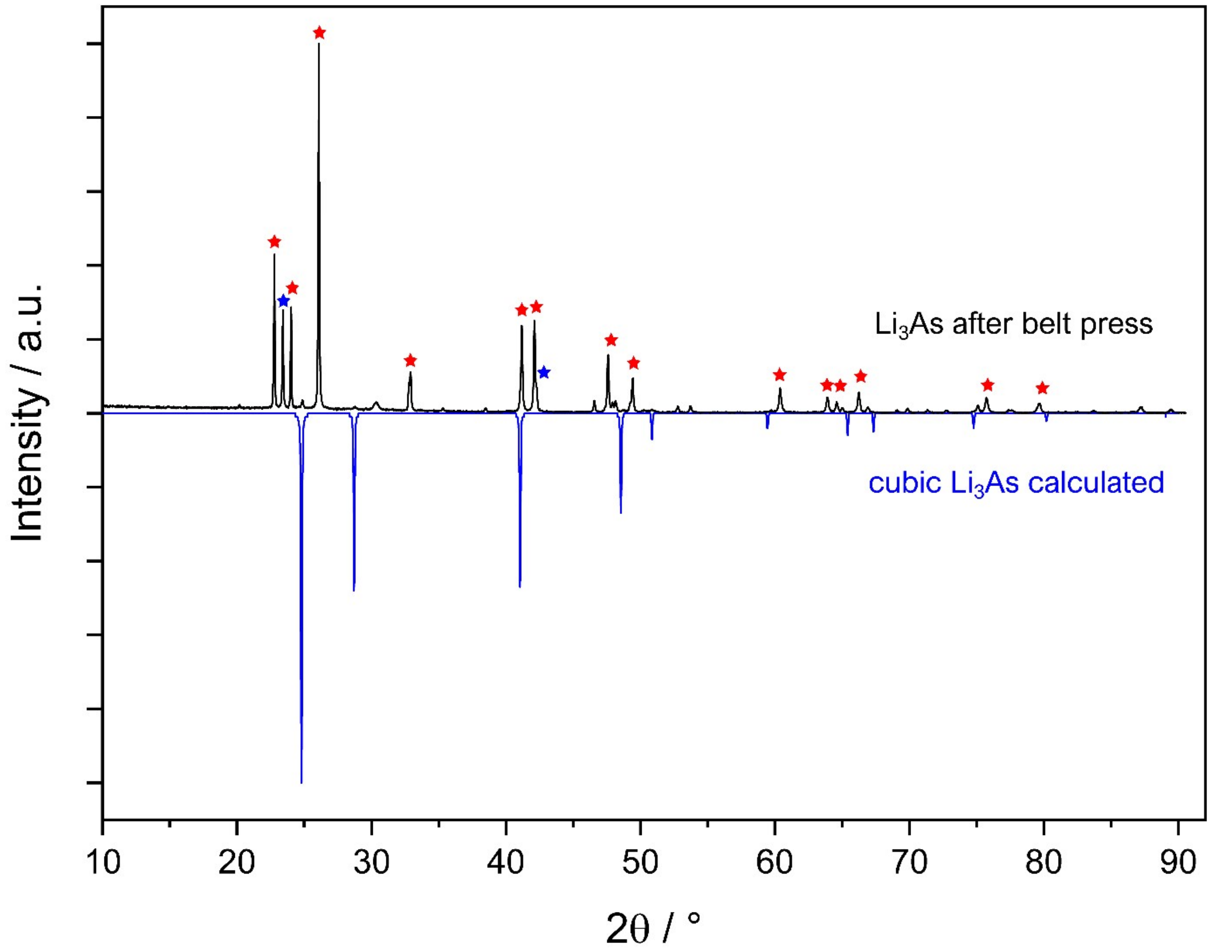


Figure S4. Powder diffractogram of Li_3As after quenching from high-pressure (3.6 GPa) and temperature (700 °C) to ambient conditions (black). Intensities marked with red stars can be assigned to hexagonal Li3As. The intensity marked in blue cannot be assigned to any phase. Negative intensities show the calculated cubic Li_3As modification in the space group $Fm\bar{3}m$ (No. 225)

3. Conductivity experiments

Lithium-ion mobility was determined via a Zahner Zennium impedance analyser connected to an inhouse built cell. All measurements and sample preparations were carried out in an argon filled Glovebox (M Braun) with oxygen and moisture levels below 0.5 ppm. The synthesized powders were pressed (6 t) to cylindrical pellets (Ø = 8 mm) obtaining pellet densities from 82 - 85% (Table S6). The cold pressed pellets were placed between two indium foils surrounded by platin electrodes connected to the impedance analyser:

(corundum // platin contact // indium foil // **sample** // indium foil // platin contact // corundum)

Please note that for the sample of Li_2Se gold foil was used instead of indium foil to contact the pellet. Two heating and two subsequent colling cycles were performed in a temperature range of 50 °C – 100 °C in steps of 10 °C with an excitation voltage of 50 mV. For each temperature the impedance was measured in a frequency range of 1 MHz to 100 mHz. To determine the specific lithium-ion conductivities of the samples data evaluation was only applied for the last cooling cycle, because estimated sintering processes via measurements led to bad data quality for the previous cycles. The impedance data of the samples at 50 °C are displayed in the corresponding Nyquist plots (Figure S3) and were analysed by fitting the measured data with an equivalent circuit. Depending on the samples different equivalent circuits were used (Table S4) and the retrieved resistance values were used to calculate the specific lithium-ion conductivity in dependence of the sample geometry and crystallographic density. Activation energies of the measured samples are displayed in Table S5.

Table S2. Lithium-ion conductivities of the solid solution in the system Li_3As – Li_2Se.

Temperature / °C	specific lithium-ion conductivity / $S \cdot cm^{-1}$			
	$Li_{2.2}As_{0.2}Se_{0.8}$	$Li_{2.4}As_{0.4}Se_{0.6}$	$Li_{2.6}As_{0.6}Se_{0.4}$	$Li_{2.8}As_{0.8}Se_{0.2}$
50	$3.1(5) \cdot 10^{-6}$	$2.1(2) \cdot 10^{-4}$	$7.6(1) \cdot 10^{-4}$	$6.0(8) \cdot 10^{-4}$
60	$2.0(6) \cdot 10^{-6}$	$3.5(9) \cdot 10^{-4}$	$1.1(8) \cdot 10^{-3}$	$9.6(3) \cdot 10^{-4}$
70	$1.4(1) \cdot 10^{-6}$	$5.5(1) \cdot 10^{-4}$	$1.7(5) \cdot 10^{-3}$	$1.5(3) \cdot 10^{-3}$
80	$8.8(1) \cdot 10^{-5}$	$7.3(6) \cdot 10^{-4}$	$2.5(5) \cdot 10^{-3}$	$2.6(5) \cdot 10^{-3}$
90	$5.3(9) \cdot 10^{-5}$	$1.1(4) \cdot 10^{-3}$	$3.7(1) \cdot 10^{-3}$	$3.9(4) \cdot 10^{-3}$
100	$3.1(8) \cdot 10^{-5}$	$1.6(3) \cdot 10^{-3}$	$5.2(9) \cdot 10^{-3}$	$6.3(3) \cdot 10^{-3}$

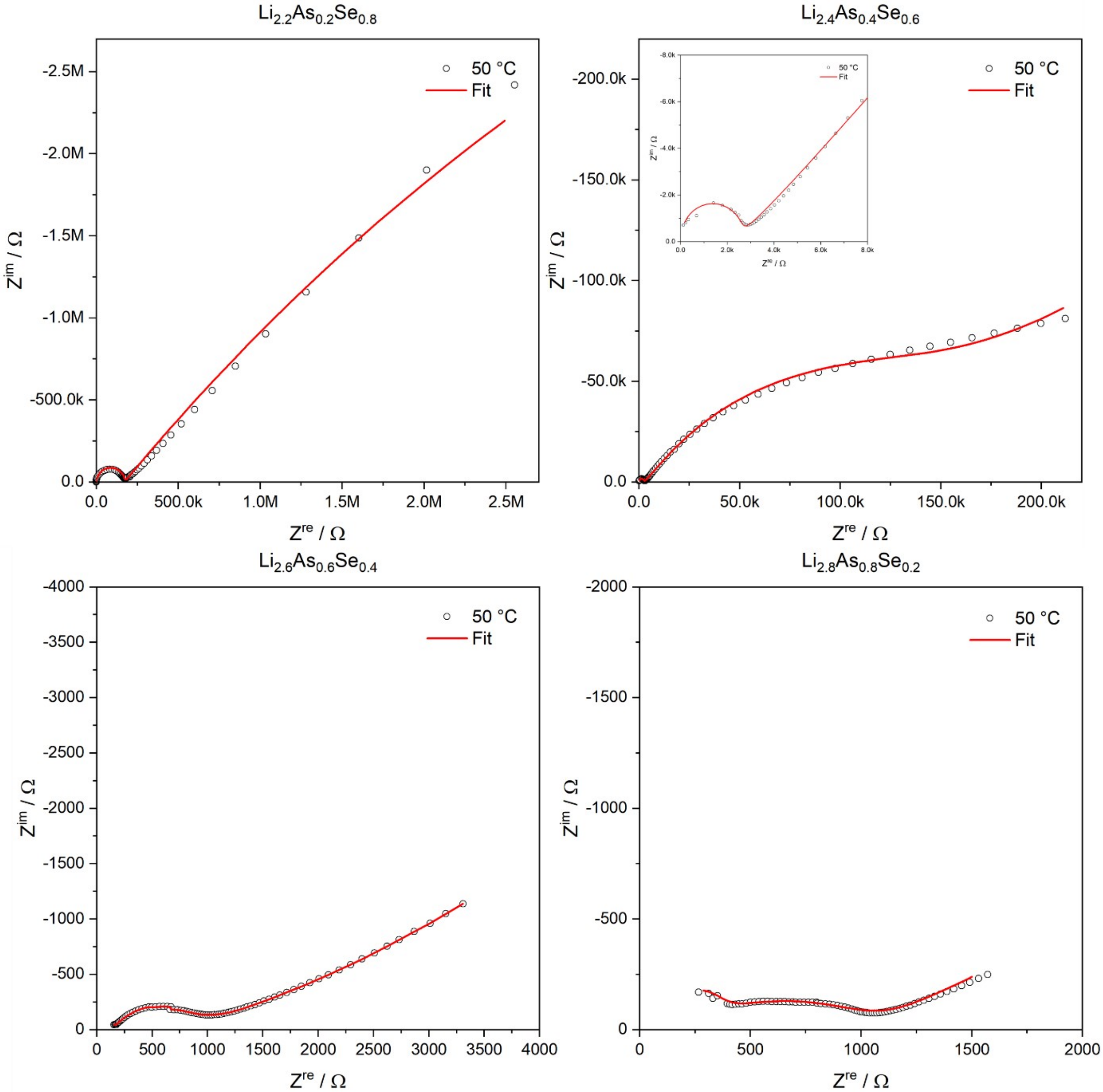


Figure S5. Nyquist plots at 50 °C of the solid solution in the system Li_3As – Li_2Se. Measured data points are displayed in black and the fitted values of the equivalent circuits are displayed in red.

Table S3. Specific lithium-ion conductivities of Li_2Se.

Temperature / °C	specific lithium-ion conductivity / $S \cdot cm^{-1}$
175	$2.9(2) \cdot 10^{-7}$
200	$1.8(9) \cdot 10^{-6}$
225	$6.0(1) \cdot 10^{-6}$
250	$2.0(5) \cdot 10^{-5}$
275	$4.3(1) \cdot 10^{-5}$
300	$7.6(5) \cdot 10^{-5}$

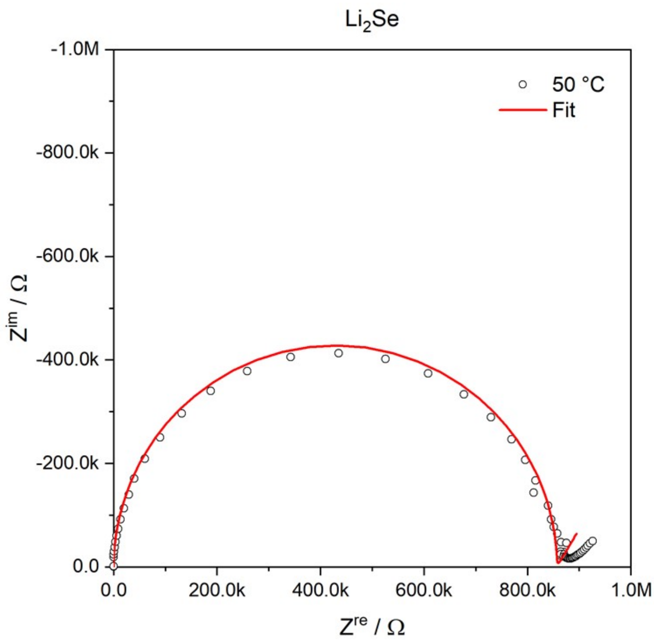


Figure S6. Nyquist plots at 175 °C of Li_2Se. Measured data points are displayed in black and the fitted values of the equivalent circuits are displayed in red.

For Li_2Se an activation energy of E_a = 0.98 eV and pellet density of 80.33% was determined.

Table S4. Equivalent circuits used for fitting the impedance data of the corresponding system.

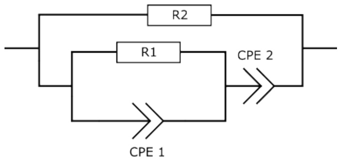
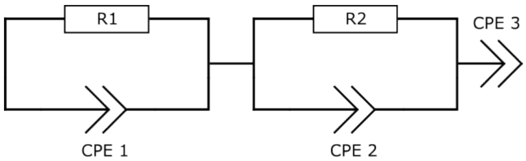
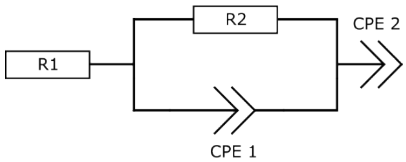
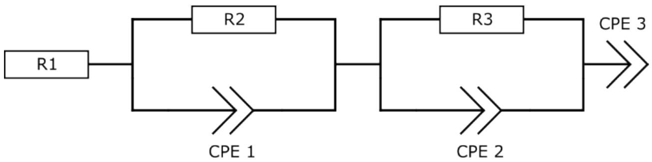
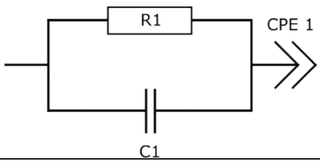
System / compound	equivalent circuit	Resistor used for conductivity determination
$Li_{2.2}As_{0.2}Se_{0.8}$		R1
$Li_{2.4}As_{0.4}Se_{0.6}$		R1
$Li_{2.6}As_{0.6}Se_{0.4}$		R2
$Li_{2.8}As_{0.8}Se_{0.2}$		R2 + R3
Li_2Se		R1

Table S5. Activation energies E_a of the solid solutions in the system Li_3As – Li_2Se.

Li_3As – Li_2Se	E_a / eV
$Li_{2.2}As_{0.2}Se_{0.8}$	0.44
$Li_{2.4}As_{0.4}Se_{0.6}$	0.41
$Li_{2.6}As_{0.6}Se_{0.4}$	0.44
$Li_{2.8}As_{0.8}Se_{0.2}$	0.47

Table S6. Pellet densities of the samples in the system Li_3As – Li_2Se.

Li_3As – Li_2Se	%
$Li_{2.2}As_{0.2}Se_{0.8}$	85.41
$Li_{2.4}As_{0.4}Se_{0.6}$	85.12
$Li_{2.6}As_{0.6}Se_{0.4}$	82.72
$Li_{2.8}As_{0.8}Se_{0.2}$	82.03