Changing the static and dynamic lattice effects for the improvement of the ionic transport properties within the argyrodite $Li_6PS_{5-x}Se_xI$

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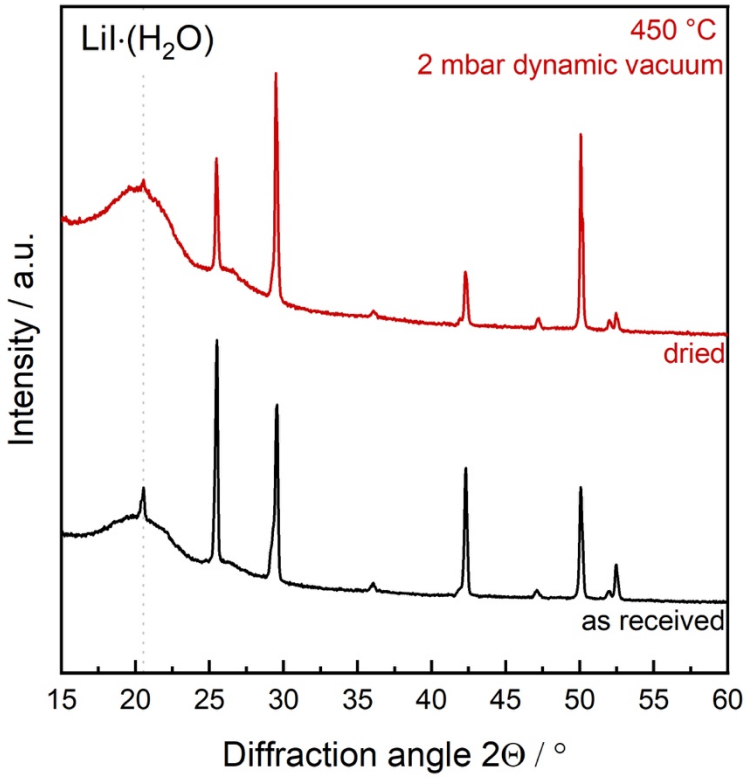

Figure S1: LiI precursor before and after a drying step. The most visible impurity reflection in the synthesized compounds is highlighted with a vertical dotted line. The drying reduced the amount of LiI·(H_2O) impurity phase, but even multiple drying steps did not result in a phase-pure precursor.

Table S1: Used constraints for the Rietveld-refinements against capillary X-Ray data. The full amount of substituted Selenium was set to the tetrahedral Wyckoff 16e site reduced by the occupancies on the remaining possible sites.

Atom	**Wyckoff position**	**Atomic coordinates**			***Occ.***	B_{iso} / Å^2
		x	***y***	***z***		
S1	4*d*	0.25	0.25	0.25	*1-(1-[1-(occ2+occ1)])-occ3*	*Var1*
Se1	4*d*	0.25	0.25	0.25	*occ3*	*Var1*
I1	4*d*	0.25	0.25	0.25	*1-[1-(occ2+occ1)]*	*Var1*
I2	4*a*	0	0	1	*1-(occ2+occ1)*	*Var2*
Se2	4*a*	0	0	1	*occ2*	*Var2*
S2	4*a*	0	0	1	*occ1*	*Var2*
S3	16*e*	*Pos*1	-*Pos*1	0.5+*Pos*1	$1-[\frac{x}{4} - 0.25 \cdot (occ2 + occ3)]$	*Var3*
Se3	16*e*	*Pos*1	-*Pos*1	0.5+*Pos*1	$\frac{x}{4} - 0.25 \cdot (occ2 + occ3)$	*Var3*
P	4*b*	0	0	0.5	1	*Var4*
Li1	24*g*	0.25	0.018	0.75	0.219	5
Li2	*48h*	0.2956	0.0266	0.7044	0.391	5

Table S2: Rietveld-refinement data of Li_6PS_5I and corresponding fit-residuals.

Li_6PS_5I

Lattice Parameter: 10.1396 (1)

R_{WP}= 5.95 %, R_{exp}= 3.66 %, Goodness of fit: 1.63

Total impurity amount: 3.5 % LiI

Atom	**Wyckoff position**	**Atomic coordinates**			***Occ.***	B_{iso} / Å^2
		x	***y***	***z***		
S1	4*d*	0.25	0.25	0.25	0.983(2)	1.35 (7)
I1	4*d*	0.25	0.25	0.25	0.017(2)	1.35 (7)
I2	4*a*	0	0	1	0.983(2)	2.10(3)
S2	4*a*	0	0	1	0.017(2)	2.10(3)
S3	16*e*	0.1162(1)	-0.1162(1)	0.6162(1)	1	1.24(4)
P	4*b*	0	0	0.5	1	0.91(5)
Li1	24*g*	0.25	0.018	0.75	0.219	5
Li2	*48h*	0.2956	0.0266	0.7044	0.391	5

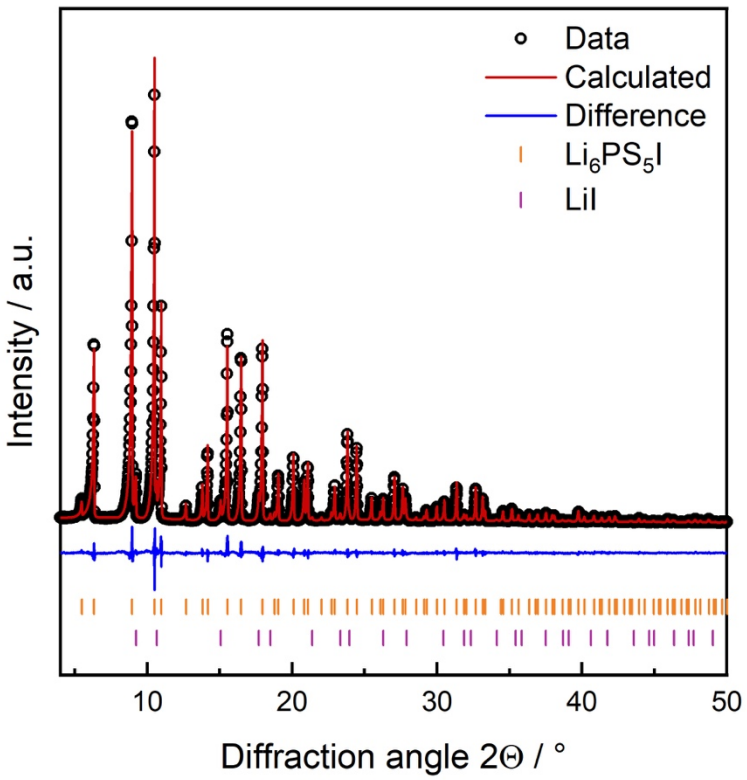

Figure S2: Diffraction pattern for Li_6PS_5I (black dots), calculated structure using a Rietveld-refinement (red line) and difference curve (blue). Minor amounts of LiI impurities can be found.

Table S3: Rietveld-refinement data of $Li_6PS_4Se_1I$ and corresponding fit-residuals.

$Li_6PS_4Se_1I$

Lattice Parameter: 10.2182(1)

R_{WP}= 5.61 %, R_{exp}= 5.27 %, Goodness of fit: 1.06

Total impurity amount: 3 % (LiI, $Li_2(S/Se)$ + $LiI(H_2O)$)

Atom	Wyckoff position	Atomic coordinates			*Occ.*	B_{iso} / Å^2
		x	*y*	*z*		
S1	4*d*	0.25	0.25	0.25	0.72(2)	1.43(8)
Se1	4*d*	0.25	0.25	0.25	0.25(2)	1.43(8)
I1	4*d*	0.25	0.25	0.25	0.03(1)	1.43(8)
I2	4*a*	0	0	1	0.97(1)	2.39(5)
Se2	4*a*	0	0	1	0.00(1)	2.39(5)
S2	4*a*	0	0	1	0.032(5)	2.39(5)
S3	16*e*	0.1176(1)	-0.1176(1)	0.6176(1)	0.813(6)	1.97(6)
Se3	16*e*	0.1176(1)	-0.1176(1)	0.6176(1)	0.187(6)	1.97(6)
P	4*b*	0	0	0.5	1	1.35(9)
Li1	24*g*	0.25	0.018	0.75	0.219	5
Li2	*48h*	0.2956	0.0266	0.7044	0.391	5

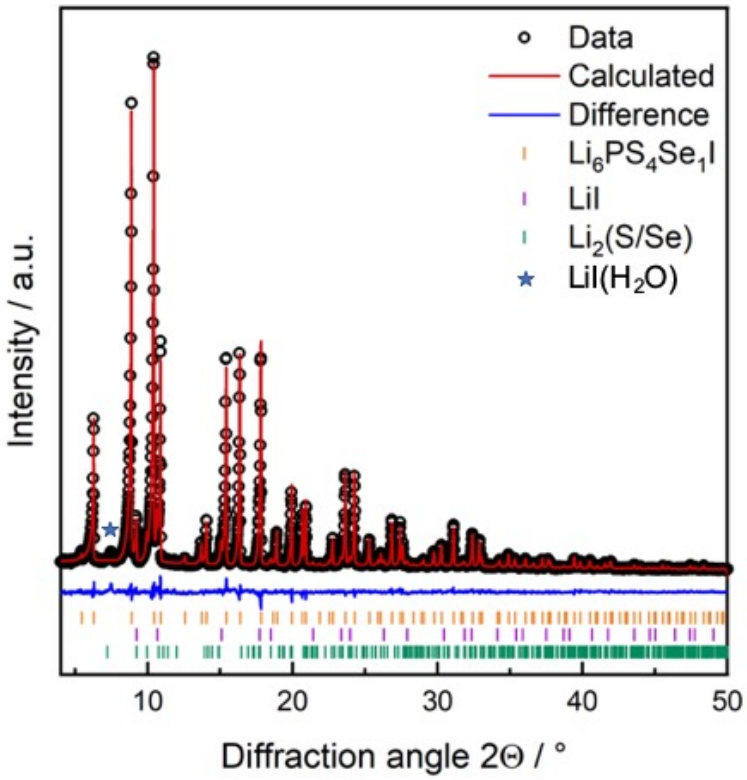

Figure S3: Diffraction pattern for $Li_6PS_4Se_1I$ (black dots), calculated structure using a Rietveld-refinement (red line) and difference curve (blue). Minor amounts of LiI (LiI·(H_2O)) and Li_2(S/Se) impurities can be found.

Table S4: Rietveld-refinement data of $Li_6PS_3Se_2I$ and corresponding fit-residuals.

$Li_6PS_3Se_2I$

Lattice Parameter: 10.3010(4)

R_{WP}= 7.37, R_{exp}= 5.39, Goodness of fit: 1.36

Total impurity amount: 3.5 % (LiI, Li_2(S/Se) + LiI(H_2O)

Atom	Wyckoff position	Atomic coordinates			*Occ.*	B_{iso} / Å^2
		x	*y*	*z*		
S1	4*d*	0.25	0.25	0.25	0.46(4)	1.4(1)
Se1	4*d*	0.25	0.25	0.25	0.47(4)	1.4(1)
I1	4*d*	0.25	0.25	0.25	0.07(2)	1.4(1)
I2	4*a*	0	0	1	0.93(2)	2.6(1)
Se2	4*a*	0	0	1	0.07(2)	2.6(1)
S2	4*a*	0	0	1	0.00(1)	2.6(1)
S3	16*e*	0.1187 (1)	-0.1187(2)	0.6187(2)	0.64(1)	1.87(8)
Se3	16*e*	0.1187 (1)	-0.1187(2)	0.6187(2)	0.36(1)	1.87(8)
P	4*b*	0	0	0.5	1	0.9(2)
Li1	24*g*	0.25	0.018	0.75	0.219	5
Li2	*48h*	0.2956	0.0266	0.7044	0.391	5

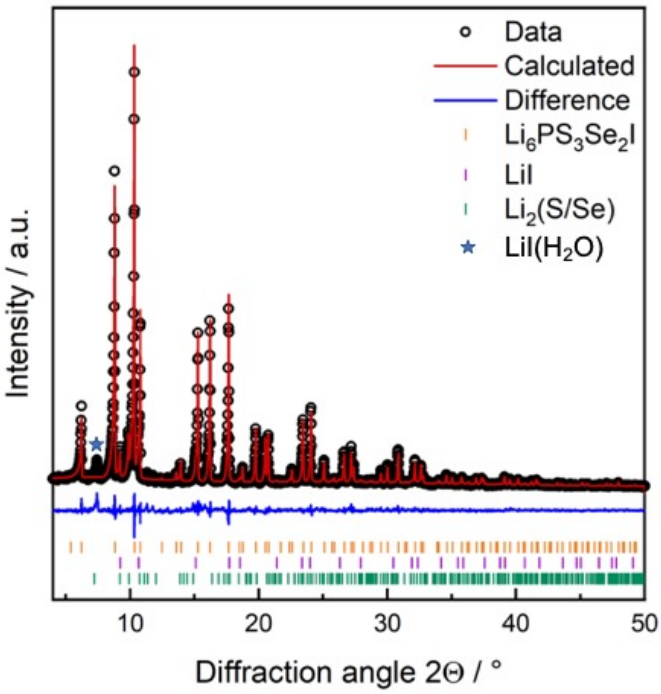

Figure S4: Diffraction pattern for $Li_6PS_3Se_2I$ (black dots), calculated structure using a Rietveld-refinement (red line) and difference curve (blue). Minor amounts of LiI ($LiI(H_2O)$) and $Li_2(S/Se)$ impurities can be found.

Table S5: Rietveld-refinement data of $Li_6PS_2Se_3I$ and corresponding fit-residuals.

$Li_6PS_2Se_3I$

Lattice Parameter: 10.3794(5)

R_{WP}= 7.21, R_{exp}= 5.37, Goodness of fit: 1.24

Total impurity amount: 2.8 % LiI+ $LiI(H_2O)$

Atom	**Wyckoff position**	**Atomic coordinates**			***Occ.***	B_{iso} / Å^2
		x	***y***	***z***		
S1	4*d*	0.25	0.25	0.25	0.23(4)	2.1 (1)
Se1	4*d*	0.25	0.25	0.25	0.72(4)	2.1 (1)
I1	4*d*	0.25	0.25	0.25	0.05(2)	2.1 (1)
I2	4*a*	0	0	1	0.95(2)	2.5(1)
Se2	4*a*	0	0	1	0.03(2)	2.5(1)
S2	4*a*	0	0	1	0.02(1)	2.5(1)
S3	16*e*	0.1200(2)	-0.1200(2)	0.6200 2)	0.44(1)	2.65(9)
Se3	16*e*	0.1200(2)	-0.1200(2)	0.6200 2)	0.56(1)	2.65(9)
P	4*b*	0	0	0.5	1	2.6 (2)
Li1	24*g*	0.25	0.018	0.75	0.219	5
Li2	*48h*	0.2956	0.0266	0.7044	0.391	5

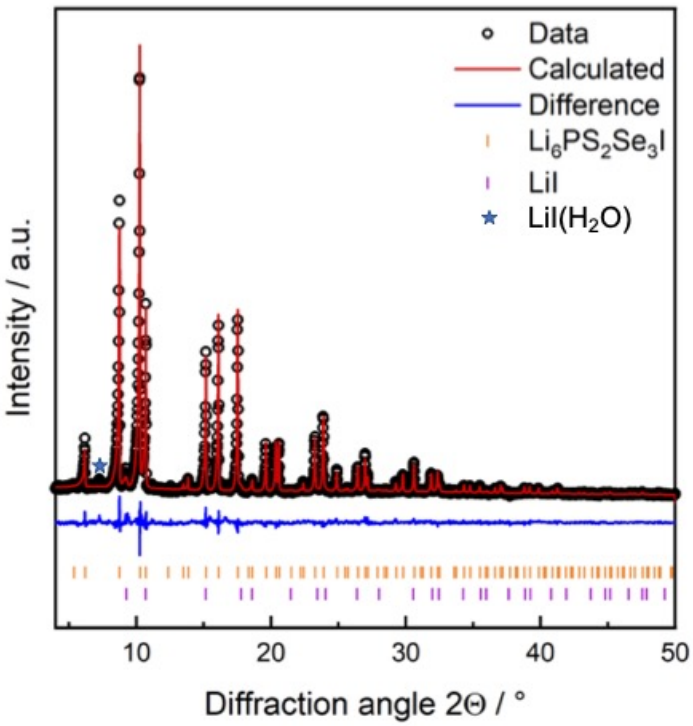

Figure S5: Diffraction pattern for $Li_6PS_2Se_3I$ (black dots), calculated structure using a Rietveld-refinement (red line) and difference curve (blue). Minor amounts of LiI ($LiI(H_2O)$) impurities can be found.

Table S6: Rietveld-refinement data of $Li_6PS_1Se_4I$ and corresponding fit-residuals.

$Li_6PS_1Se_4I$

Lattice Parameter: 10.4625(7)

R_{WP}= 6.71, R_{exp}= 6.07, Goodness of fit: 1.11

Total impurity amount: 3 % LiI

Atom	**Wyckoff position**	**Atomic coordinates**			***Occ.***	B_{iso} / Å^2
		x	***y***	***z***		
S1	4*d*	0.25	0.25	0.25	0.25(4)	2.1 (2)
Se1	4*d*	0.25	0.25	0.25	0.75(4)	2.1 (2)
I1	4*d*	0.25	0.25	0.25	0.07(2)	2.1 (2)
I2	4*a*	0	0	1	0.93(2)	2.4(1)
Se2	4*a*	0	0	1	0.07(2)	2.4(1)
S2	4*a*	0	0	1	0.00(1)	2.4(1)
S3	16*e*	0.1202(2)	-0.1202(2)	0.6202(2)	0.20(1)	2.72(8)
Se3	16*e*	0.1202(2)	-0.1202(2)	0.6202(2)	0.80(1)	2.72(8)
P	4*b*	0	0	0.5	1	3.3 (3)
Li1	24*g*	0.25	0.018	0.75	0.219	5
Li2	*48h*	0.2956	0.0266	0.7044	0.391	5

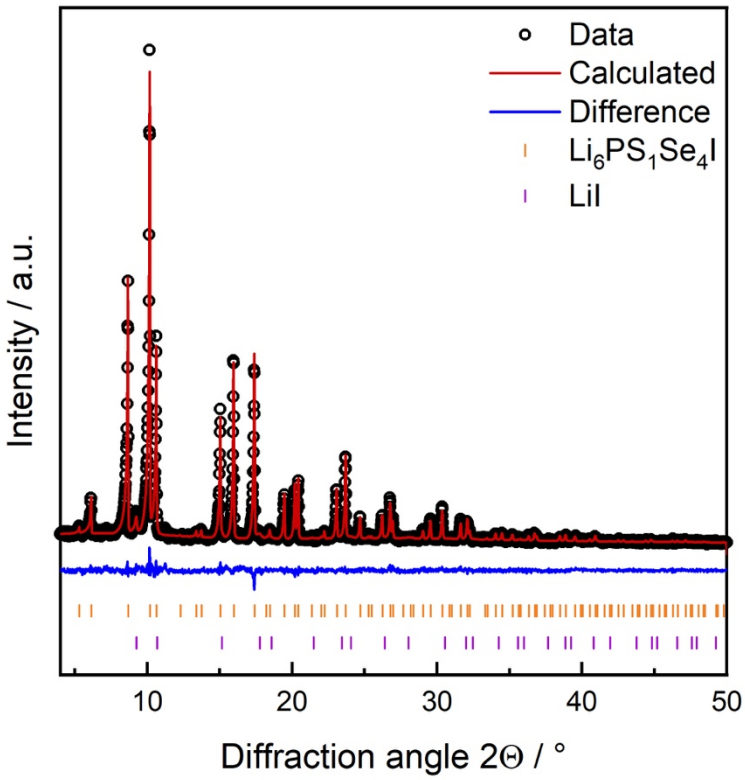

Figure S6: Diffraction pattern for $Li_6PS_1Se_4I$ (black dots), calculated structure using a Rietveld-refinement (red line) and difference curve (blue). Minor amounts of LiI impurities can be found.

Table S7: Rietveld-refinement data of Li_6PSe_5I and corresponding fit-residuals.

Li_6PSe_5I

Lattice Parameter: 10.5515(8)

R_{WP}= 6.74, R_{exp}= 6.66, Goodness of fit: 1.01

Total impurity amount: 3 % LiI

Atom	Wyckoff position	Atomic coordinates			*Occ.*	B_{iso} / Å^2
		x	*y*	*z*		
Se1	4*d*	0.25	0.25	0.25	0.97(4)	1.9 (2)
I1	4*d*	0.25	0.25	0.25	0.03(2)	1.9 (2)
I2	4*a*	0	0	1	0.97(4)	3.1(2)
Se2	4*a*	0	0	1	0.03(2)	3.1(2)
Se3	16*e*	0.1205(2)	-0.1205(2)	0.6205(2)	1	2.45(5)
P	4*b*	0	0	0.5	1	1.6 (2)
Li1	24*g*	0.25	0.018	0.75	0.219	5
Li2	*48h*	0.2956	0.0266	0.7044	0.391	5

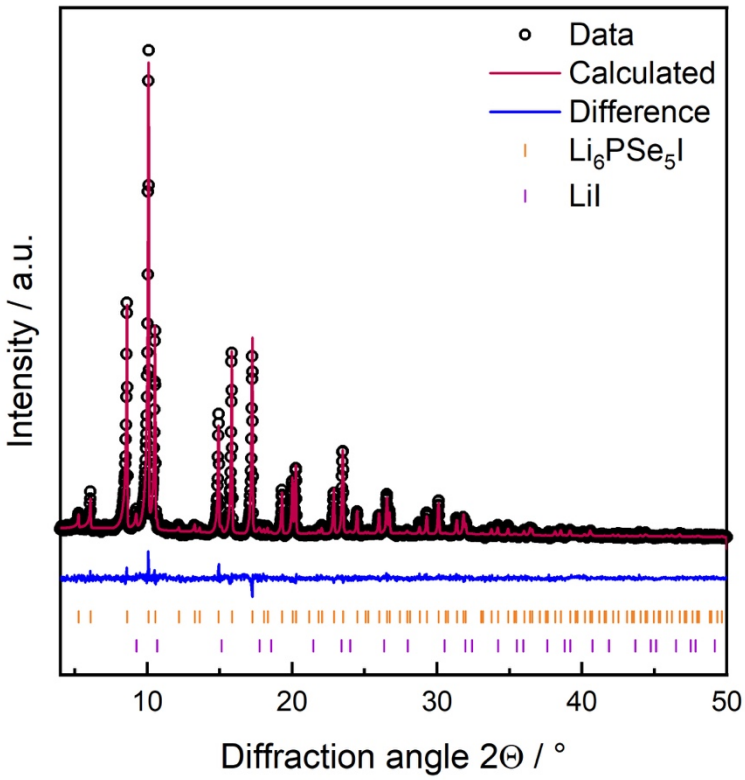

Figure S7: Diffraction pattern for Li_6PSe_5I (black dots), calculated structure using a Rietveld-refinement (red line) and difference curve (blue). Minor amounts of LiI impurities can be found.

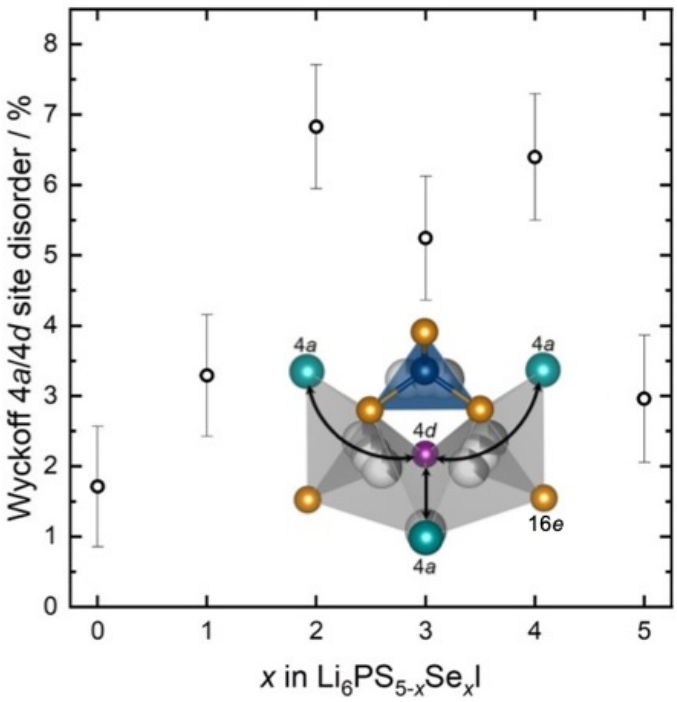

Figure S8: Site-disorder between the Wyckoff 4d and 4a site as obtained from Rietveld-Refinements. The large amount of necessary constraints makes a Rietveld-Refinement difficult and the here shown values represent a general trend, rather than absolute values. No direct correlation between the site-disorder and transport properties could be observed.