

Sodium Filling in Superadamantoide Na_{1.36}(Si_{0.86}Ga_{0.14})₂As_{2.98} and the Mixed Valent Arsenidosilicate-Silicide Li_{1.5}Ga_{0.9}Si_{3.1}As₄

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Table S1. Crystallographic data for the Rietveld refinement of Na_{1.36}(Si_{0.86}Ga_{0.14})₂As_{2.98}.

Formula	Na _{1.36} (Si _{0.86} Ga _{0.14}) ₂ As _{2.98}
formula mass/g mol ⁻¹	322.59
space group	<i>I</i> 4 ₁ / <i>a</i> (no. 88)
<i>a</i> /Å	19.8742(3)
<i>c</i> /Å	37.760(1)
<i>V</i> _{cell} /Å ³	14914.4(6)
<i>Z</i>	100
$\rho_{x\text{-ray}}$ /g cm ⁻³	3.592
<i>R</i> _{exp} / <i>R</i> _{Bragg}	6.469 / 2.138
<i>R</i> _p / <i>R</i> _{wp}	6.748 / 8.761
Goof	1.354

Table S2. Fractional atomic coordinates and equivalent displacement parameters of Na_{1.36}(Si_{0.86}Ga_{0.14})₂As_{2.98}.

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	<i>U</i> _{eq} / Å ²
As01	16 <i>f</i>	0.05638(2)	0.33401(2)	0.51733(2)	1	0.01111(5)
As02	16 <i>f</i>	0.07131(2)	0.20675(2)	0.59410(2)	1	0.01065(5)
As03	16 <i>f</i>	0.01081(2)	0.11520(2)	0.05048(2)	1	0.01088(5)
As04	16 <i>f</i>	0.11196(2)	0.56251(2)	0.33846(2)	1	0.01078(5)
As05	16 <i>f</i>	0.26618(2)	0.40360(2)	0.05532(2)	1	0.01083(5)
As06	16 <i>f</i>	0.13571(2)	0.12675(2)	0.27105(2)	1	0.01107(5)
As07	16 <i>f</i>	0.47134(2)	0.53560(2)	0.08725(2)	1	0.01079(5)
As08	16 <i>f</i>	0.10405(2)	0.06751(2)	0.51582(2)	1	0.01127(5)
As09	16 <i>f</i>	0.34218(2)	0.50505(2)	0.15927(2)	1	0.01087(5)
As10	16 <i>f</i>	0.14659(2)	0.11857(2)	0.12386(2)	1	0.01126(5)
As11	16 <i>f</i>	0.23797(2)	0.04108(2)	0.01810(2)	1	0.01322(6)
As12	16 <i>f</i>	0.21841(2)	0.23934(2)	0.51532(2)	1	0.01176(5)
As13	16 <i>f</i>	0.27458(2)	0.13594(2)	0.19919(2)	1	0.01358(6)
As14	16 <i>f</i>	0.36688(2)	0.06628(2)	0.08744(2)	1	0.01403(6)
As15	16 <i>f</i>	0.27414(2)	0.26501(2)	0.12759(2)	1	0.01578(6)
As16	16 <i>f</i>	0.07962(2)	0.20554(2)	0.44485(2)	1	0.01788(6)

As17	16f	0.00742(2)	0.39800(2)	0.34197(2)	1	0.01668(6)
As18	4a	0.0000	0.2500	0.1250	0.582(3)	0.0088(3)
As19	8e	0.0000	0.2500	0.27207(2)	1	0.01874(8)
As20	16f	0.14303(2)	0.24766(2)	0.04984(2)	1	0.01182(5)
Na01	16f	0.27010(7)	0.03280(7)	0.14333(4)	1	0.0277(3)
Na02	16f	0.35000(7)	0.54122(7)	0.03256(4)	1	0.0326(3)
Na03	16f	0.12885(7)	0.00909(7)	0.06947(4)	1	0.0295(3)
Na04	8c	0.0000	0.0000	0.0000	1	0.0462(6)
Na05	16f	0.48769(8)	0.08246(9)	0.04290(5)	1	0.0459(4)
Na06	16f	0.11713(8)	0.11324(8)	0.38726(4)	1	0.0409(4)
Na07	16f	0.41014(9)	0.09933(13)	0.22964(5)	1	0.0641(6)
Na08	16f	0.29738(11)	0.18381(9)	0.05745(5)	1	0.0558(5)
Na09	16f	0.1017(2)	0.2786(2)	0.33180(16)	0.666(4)	0.1143(17)
Na10	16f	0.4101(4)	0.2009(4)	0.1215(3)	0.334(4)	0.1143(17)
Ga01	16f	0.15729(3)	0.14666(3)	0.62309(2)	0.218(2)	0.00978(16)
Si01	16f	0.15729(3)	0.14666(3)	0.62309(2)	0.782(2)	0.00978(16)
Ga02	16f	0.13310(3)	0.27538(3)	0.55496(2)	0.198(2)	0.00972(17)
Si02	16f	0.13310(3)	0.27538(3)	0.55496(2)	0.802(2)	0.00972(17)
Ga03	16f	0.34216(3)	0.34344(3)	0.01705(2)	0.148(3)	0.01120(18)
Si03	16f	0.34216(3)	0.34344(3)	0.01705(2)	0.852(3)	0.01120(18)
Ga04	16f	0.06934(2)	0.04494(2)	0.30432(2)	0.401(3)	0.01096(14)
Si04	16f	0.06934(2)	0.04494(2)	0.30432(2)	0.599(3)	0.01096(14)
Ga05	16f	0.07343(2)	0.05024(2)	0.16041(2)	0.317(2)	0.01055(15)
Si05	16f	0.07343(2)	0.05024(2)	0.16041(2)	0.683(2)	0.01055(15)
Ga06	16f	0.02873(2)	0.12330(2)	0.55560(2)	0.252(3)	0.01014(16)
Si06	16f	0.02873(2)	0.12330(2)	0.55560(2)	0.748(3)	0.01014(16)
Ga07	16f	0.07321(3)	0.18635(3)	0.08887(2)	0.202(3)	0.00963(17)
Si07	16f	0.07321(3)	0.18635(3)	0.08887(2)	0.798(3)	0.00963(17)
Si08	8e	0.0000	0.2500	0.48339(3)	1	0.00879(17)
Si09	16f	0.44600(3)	0.01490(3)	0.12449(2)	1	0.00863(12)
Si10	16f	0.20756(3)	0.06330(3)	0.23320(2)	1	0.00841(12)
Si11	16f	0.20322(3)	0.19582(3)	0.16135(2)	1	0.00951(13)
Si12	16f	0.18509(3)	0.01724(3)	0.55352(2)	1	0.00970(12)
Si13	16f	0.06228(3)	0.18664(3)	0.23246(2)	1	0.00573(11)

Table S3. Anisotropic displacement parameters of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$.

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
As01	0.01184(12)	0.01051(11)	0.01098(12)	0.00107(9)	-0.00094(9)	-0.00006(9)
As02	0.01071(11)	0.01044(11)	0.01081(12)	0.00070(8)	0.00059(9)	-0.00051(9)
As03	0.01070(11)	0.00985(11)	0.01209(12)	-0.00074(8)	-0.00037(9)	-0.00043(9)
As04	0.00988(11)	0.01126(11)	0.01118(12)	0.00001(8)	0.00018(9)	0.00154(9)
As05	0.01066(11)	0.01047(11)	0.01137(12)	0.00186(8)	-0.00060(9)	-0.00031(9)
As06	0.00971(11)	0.01226(11)	0.01125(12)	0.00187(9)	-0.00114(9)	0.00002(9)
As07	0.01069(11)	0.01062(11)	0.01105(12)	0.00139(8)	-0.00054(9)	-0.00009(9)
As08	0.01068(11)	0.01149(11)	0.01162(12)	0.00167(8)	0.00003(9)	-0.00055(9)
As09	0.01062(11)	0.01033(11)	0.01165(12)	0.00101(8)	0.00078(9)	0.00035(9)
As10	0.01105(11)	0.01037(11)	0.01236(12)	-0.00068(8)	-0.00148(9)	-0.00056(9)
As11	0.01377(12)	0.00978(11)	0.01610(13)	0.00086(9)	-0.00550(10)	-0.00036(9)
As12	0.01078(11)	0.01299(12)	0.01151(12)	0.00110(9)	0.00039(9)	-0.00089(9)
As13	0.00952(11)	0.01422(12)	0.01702(13)	-0.00057(9)	-0.00223(10)	0.00544(10)

As14	0.01486(12)	0.00967(11)	0.01758(14)	0.00109(9)	-0.00601(10)	0.00016(10)
As15	0.01343(12)	0.01567(13)	0.01823(14)	-0.00291(9)	0.00136(10)	0.00498(10)
As16	0.01665(13)	0.02342(14)	0.01358(13)	0.00720(10)	0.00170(10)	-0.00391(11)
As17	0.01822(13)	0.01365(12)	0.01817(14)	-0.00101(10)	-0.00449(11)	-0.00295(10)
As18	0.0086(3)	0.0086(3)	0.0092(5)	0.000	0.000	0.000
As19	0.0224(2)	0.0212(2)	0.01263(18)	0.01134(15)	0.000	0.000
As20	0.01161(12)	0.01180(12)	0.01205(12)	-0.00090(9)	0.00039(9)	0.00046(9)
Na01	0.0247(6)	0.0284(7)	0.0301(7)	0.0085(5)	0.0050(5)	-0.0037(5)
Na02	0.0297(7)	0.0342(7)	0.0340(8)	0.0009(6)	-0.0042(6)	-0.0178(6)
Na03	0.0299(7)	0.0300(7)	0.0287(7)	-0.0003(5)	0.0075(6)	-0.0093(6)
Na04	0.0399(12)	0.0530(14)	0.0457(13)	-0.0152(10)	0.0183(10)	-0.0333(11)
Na05	0.0300(8)	0.0547(10)	0.0528(10)	0.0006(7)	0.0024(7)	0.0370(8)
Na06	0.0354(8)	0.0495(9)	0.0377(8)	0.0100(7)	-0.0075(7)	-0.0252(7)
Na07	0.0267(8)	0.1194(19)	0.0463(11)	0.0136(10)	-0.0034(7)	0.0012(11)
Na08	0.0872(14)	0.0357(9)	0.0445(10)	0.0278(9)	0.0049(10)	0.0103(8)
Na09	0.068(2)	0.076(2)	0.200(4)	0.0101(17)	-0.073(3)	0.038(3)
Na10	0.068(2)	0.076(2)	0.200(4)	0.0101(17)	-0.073(3)	0.038(3)
Ga01	0.0102(3)	0.0098(3)	0.0093(3)	-0.00061(17)	0.00062(18)	-0.00043(18)
Si01	0.0102(3)	0.0098(3)	0.0093(3)	-0.00061(17)	0.00062(18)	-0.00043(18)
Ga02	0.0099(3)	0.0087(3)	0.0106(3)	0.00109(17)	-0.00047(19)	-0.00097(18)
Si02	0.0099(3)	0.0087(3)	0.0106(3)	0.00109(17)	-0.00047(19)	-0.00097(18)
Ga03	0.0099(3)	0.0124(3)	0.0113(3)	0.00198(19)	0.0013(2)	-0.0013(2)
Si03	0.0099(3)	0.0124(3)	0.0113(3)	0.00198(19)	0.0013(2)	-0.0013(2)
Ga04	0.0106(2)	0.0115(2)	0.0108(2)	-0.00018(14)	0.00096(15)	0.00098(16)
Si04	0.0106(2)	0.0115(2)	0.0108(2)	-0.00018(14)	0.00096(15)	0.00098(16)
Ga05	0.0102(2)	0.0105(2)	0.0110(3)	0.00034(16)	-0.00178(16)	0.00052(17)
Si05	0.0102(2)	0.0105(2)	0.0110(3)	0.00034(16)	-0.00178(16)	0.00052(17)
Ga06	0.0097(2)	0.0102(2)	0.0106(3)	0.00098(16)	0.00068(18)	0.00049(18)
Si06	0.0097(2)	0.0102(2)	0.0106(3)	0.00098(16)	0.00068(18)	0.00049(18)
Ga07	0.0095(3)	0.0090(3)	0.0103(3)	-0.00185(17)	-0.00147(18)	0.00114(18)
Si07	0.0095(3)	0.0090(3)	0.0103(3)	-0.00185(17)	-0.00147(18)	0.00114(18)
Si08	0.0085(4)	0.0087(4)	0.0092(4)	0.0031(3)	0.000	0.000
Si09	0.0080(3)	0.0089(3)	0.0089(3)	0.0005(2)	-0.0007(2)	-0.0004(2)
Si10	0.0080(3)	0.0085(3)	0.0087(3)	0.0002(2)	-0.0005(2)	0.0006(2)
Si11	0.0093(3)	0.0091(3)	0.0102(3)	-0.0003(2)	-0.0006(2)	0.0014(2)
Si12	0.0094(3)	0.0093(3)	0.0104(3)	0.0005(2)	0.0007(2)	-0.0005(2)
Si13	0.0062(3)	0.0054(3)	0.0056(3)	0.0028(2)	-0.0007(2)	0.0005(2)

Table S4. Crystallographic data for the Rietveld refinement of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$.

Formula	$\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$
formula mass/g mol ⁻¹	460.00
space group	C2/c (no.15)
<i>a</i> /Å	10.9201(5)
<i>b</i> /Å	10.9302(5)
<i>c</i> /Å	13.1496(5)
β/deg	101.959(7)
$V_{\text{cell}}/\text{\AA}^3$	1535.5(1)
<i>Z</i>	8
$\rho_{x\text{-ray}}/\text{g cm}^{-3}$	3.979
$R_{\text{exp}}/R_{\text{Bragg}}$	6.392 / 4.492
$R_{\text{p}}/R_{\text{wp}}$	9.636 / 13.956

GooF	2.183
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Table S5. Fractional atomic coordinates and equivalent displacement parameters of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$.

Atom	Wyckoff position	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy	<i>U</i> _{eq} / Å ²
As01	8 <i>f</i>	0.14351(14)	0.05219(13)	0.36284(10)	1	0.0099(3)
As02	8 <i>f</i>	0.10672(14)	0.30203(13)	0.13653(10)	1	0.0105(3)
As03	8 <i>f</i>	0.41389(14)	0.32274(13)	0.36286(11)	1	0.0092(3)
As04	8 <i>f</i>	0.33568(14)	0.07293(13)	0.13680(11)	1	0.0096(3)
Ga01	4 <i>e</i>	0.0000	0.1856(4)	0.2500	0.458(16)	0.0097(10)
Si01	4 <i>e</i>	0.0000	0.1856(4)	0.2500	0.542(16)	0.0097(10)
Ga02	8 <i>f</i>	0.25088(11)	0.4362(3)	0.25002(8)	0.451(15)	0.0096(9)
Si02	8 <i>f</i>	0.25088(11)	0.4362(3)	0.25002(8)	0.549(15)	0.0096(9)
Ga03	4 <i>e</i>	0.0000	0.6874(4)	0.2500	0.448(16)	0.0101(10)
Si03	4 <i>e</i>	0.0000	0.6874(4)	0.2500	0.552(16)	0.0101(10)
Si04	8 <i>f</i>	0.0491(2)	0.4375(2)	0.44776(17)	1	0.0062(5)
Si05	8 <i>f</i>	0.2994(2)	0.1873(2)	0.44789(17)	1	0.0057(5)
Li01	8 <i>f</i>	0.075(6)	0.066(6)	0.018(4)	0.73(9)	0.09(3)
Li02	8 <i>f</i>	0.321(8)	0.310(8)	0.007(5)	0.75(10)	0.13(4)

Table S6. Anisotropic displacement parameters of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$.

Atom	<i>U</i> ¹¹	<i>U</i> ²²	<i>U</i> ³³	<i>U</i> ¹²	<i>U</i> ¹³	<i>U</i> ²³
As01	0.0104(6)	0.0108(6)	0.0071(5)	-0.0033(4)	-0.0014(4)	-0.0020(4)
As02	0.0101(6)	0.0108(6)	0.0090(5)	0.0003(4)	-0.0016(4)	0.0024(4)
As03	0.0095(6)	0.0107(5)	0.0073(5)	-0.0044(4)	0.0017(4)	0.0015(4)
As04	0.0098(6)	0.0109(6)	0.0087(5)	0.0009(4)	0.0032(4)	-0.0022(4)
Ga01	0.0082(18)	0.0105(18)	0.0086(17)	0.000	-0.0027(15)	0.000
Si01	0.0082(18)	0.0105(18)	0.0086(17)	0.000	-0.0027(15)	0.000
Ga02	0.0092(17)	0.0096(17)	0.0088(17)	0.0007(4)	-0.0010(14)	0.0033(4)
Si02	0.0092(17)	0.0096(17)	0.0088(17)	0.0007(4)	-0.0010(14)	0.0033(4)
Ga03	0.0109(19)	0.0108(18)	0.0091(18)	0.000	0.0031(16)	0.000
Si03	0.0109(19)	0.0108(18)	0.0091(18)	0.000	0.0031(16)	0.000
Si04	0.0079(10)	0.0087(10)	0.0014(9)	0.0004(7)	-0.0006(8)	-0.0005(8)
Si05	0.0075(11)	0.0079(10)	0.0012(9)	-0.0008(7)	-0.0006(8)	-0.0002(8)
Li01	0.10(4)	0.10(5)	0.07(3)	0.05(4)	0.01(3)	-0.04(3)
Li02	0.15(7)	0.18(8)	0.05(3)	0.04(5)	0.01(4)	0.00(4)

Table S7. Elemental analysis of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ by EDX; signals of oxygen were not taken into account due to hydrolysis.

$\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$	Na	Ga	Si	As
Calculated / atom-%	21.5	4.4	27.1	47.0
Measured / atom-%	23.9(1)	5.2(1)	25.9(1)	45.0(1)

Table S8. Elemental analysis of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ by EDX; signals of oxygen were not taken into account due to hydrolysis.

$\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$	Ga	Si	As
Calculated / atom-%	11.3	38.8	50.0
Measured / atom-%	11.8(1)	41.0(1)	47.2(1)

The partial electronic conductivity of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ and $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ were determined by potentiostatic polarization measurements. The corresponding *I/t* and *I/U* curves are shown in Figures S1 and S2 for $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ and Figures S3 and S4 for $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$.

For $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$ and voltages >0.3 V, instead of a current equilibrium, a constant increase in current was recorded. The current increase might be due to sample decomposition, which is why for $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$, lower voltages of up to 0.25 V were used. This phenomenon was not observed for $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$ for voltages up to 0.5 V

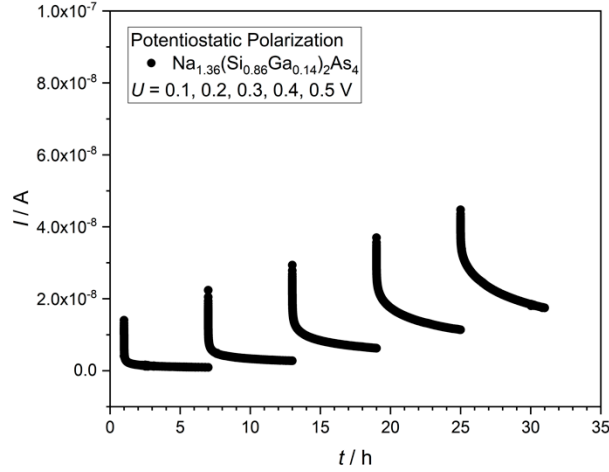


Figure S1. I/t curve for the determination of the electronic conductivity of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$. Voltages of 0.1, 0.2, 0.3, 0.4, and 0.5 V were applied for 6 h each, with the current being recorded.

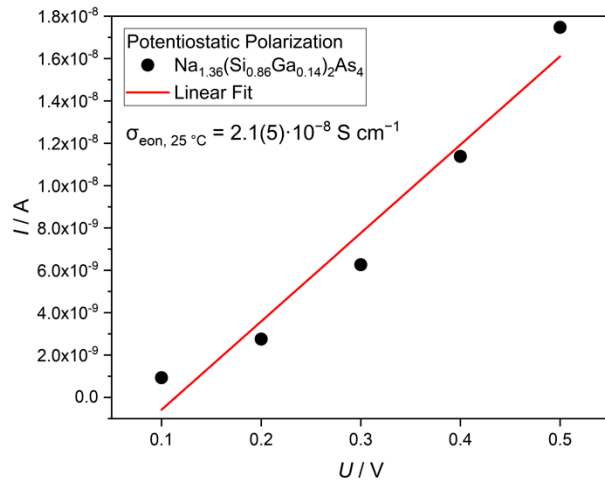


Figure S2. I/U curve for the determination of the electronic conductivity of $\text{Na}_{1.36}(\text{Si}_{0.86}\text{Ga}_{0.14})_2\text{As}_{2.98}$. The current was taken from potentiostatic polarization measurements after equilibrium. The resistance was calculated using Ohm's law, leading to a partial electronic conductivity of $2.1(5) \cdot 10^{-8} \text{ S cm}^{-1}$.

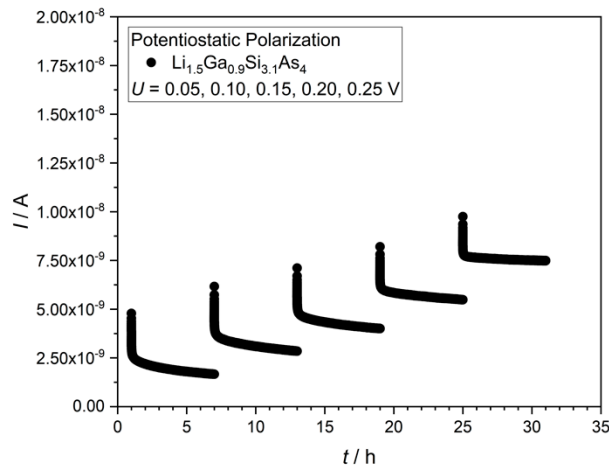


Figure S3. I/t curve for the determination of the electronic conductivity of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$. Voltages of 0.05, 0.10, 0.15, 0.20, and 0.25 V were applied for 6 h each, with the current being recorded.

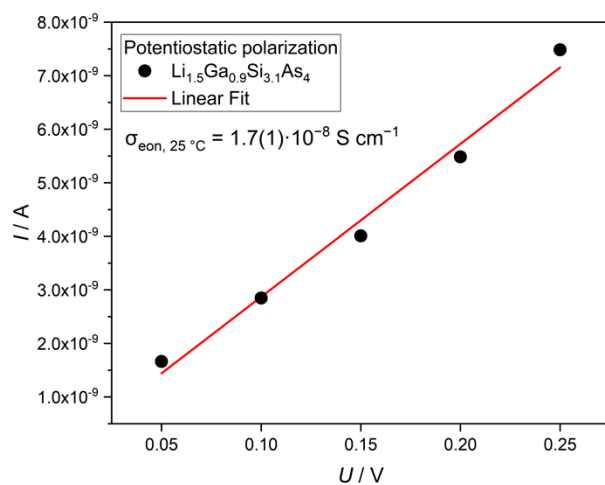


Figure S4. I/U curve for the determination of the electronic conductivity of $\text{Li}_{1.5}\text{Ga}_{0.9}\text{Si}_{3.1}\text{As}_4$. The current was taken from potentiostatic polarization measurements after equilibrium. The resistance was calculated using Ohm's law, leading to a partial electronic conductivity of $1.7(1) \cdot 10^{-8} \text{ S cm}^{-1}$.