Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Anisotropic Oxygen Ion Conduction in Melilite Intermediate Temperature Electrolytes

*Fengxia Wei, Hripsime Gasparyan, Philip Keenan, Matthias Gutmann, Yanan Fang, Tom Baikie, John Claridg,[c] Peter Slater, Christian Kloc, Tim White**

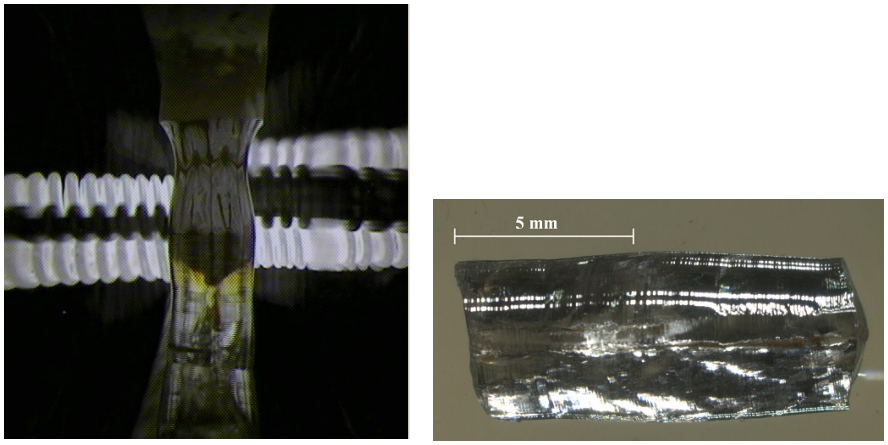

Figure S1. (a) The crystal growth inside the mirror furnace. (b) As grown melilite single crystal (composition $[LaSr]_2[Ga]_2[Ga_2O_7]_2$).

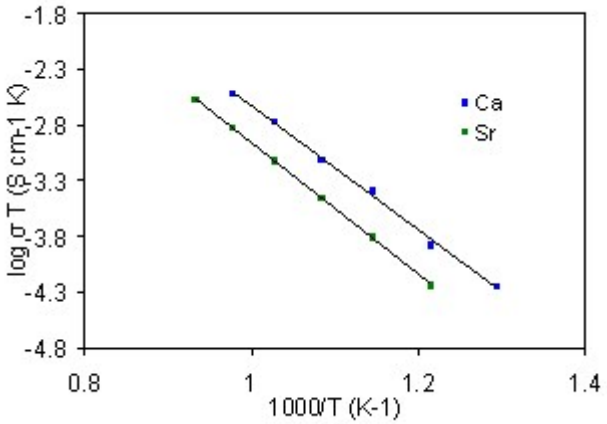

Figure S2. Conductivity for $[NdCa]_2[Ga]_2[Ga_2O_7]_2$ and $[NdSr]_2[Ga]_2[Ga_2O_7]_2$ powder pellets.

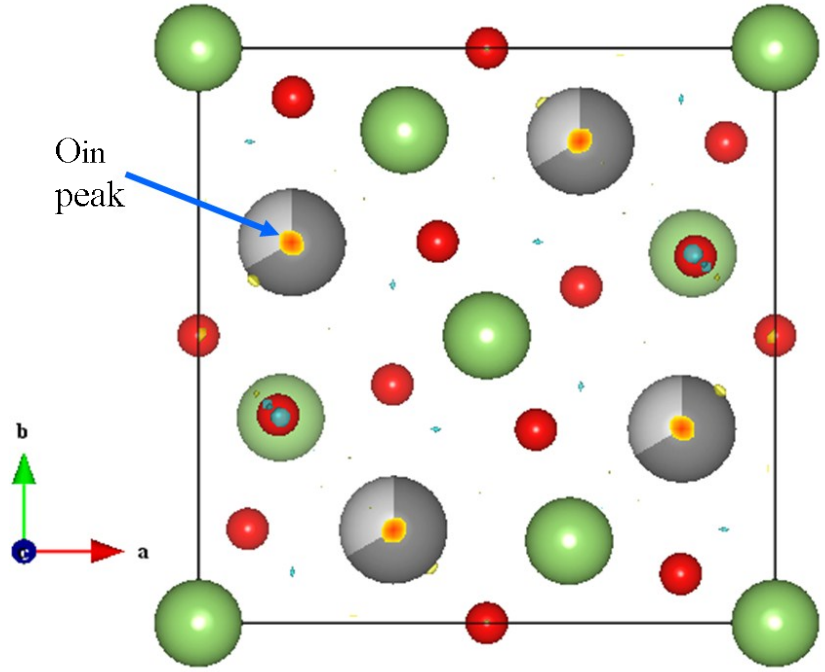

Figure S3. Single crystal neutron diffraction shows clear nuclear density suggesting the interstitial position, which is consistent with the single crystal X-ray result.

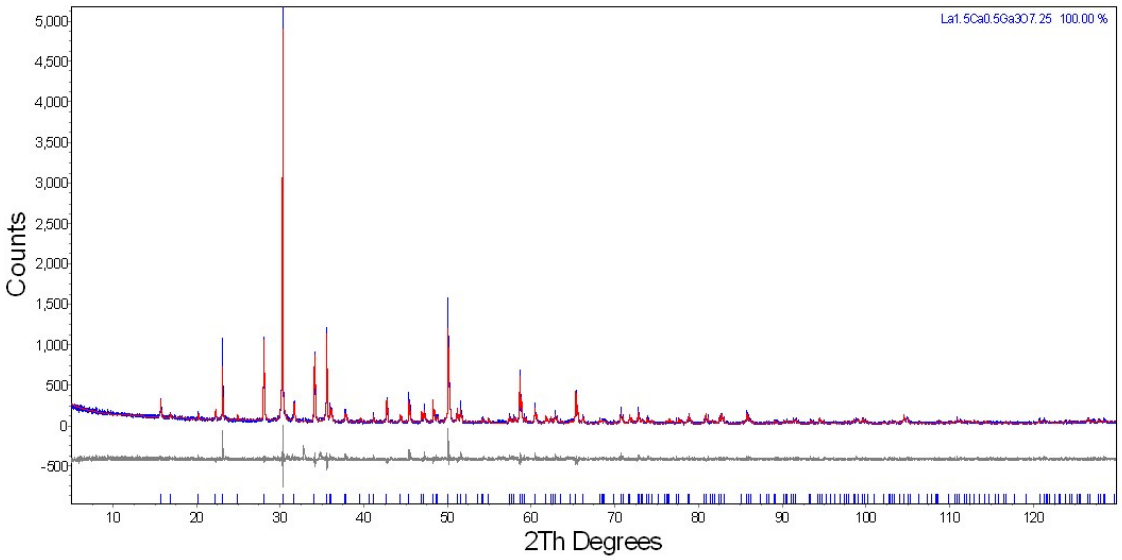

Figure S4. The powder X-ray diffraction pattern for $[La_{1.5}Ca_{0.5}]_2[Ga]_2[Ga_2O_{7.25}]_2$.

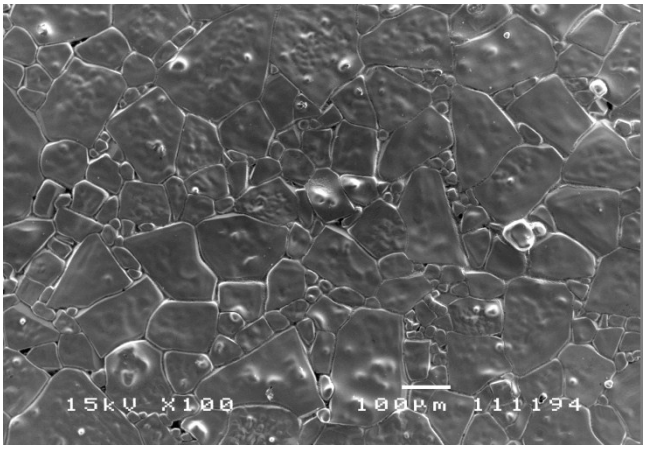

Figure S5. The SEI for as-sintered $[La_{1.5}Ca_{0.5}]_2[Ga]_2[Ga_2O_{7.25}]_2$.

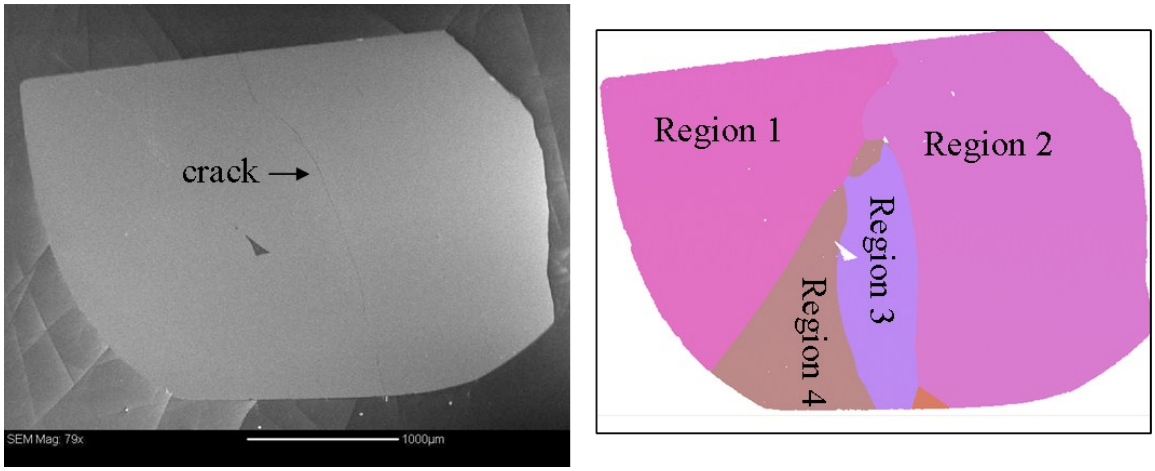

Figure S6. The seed crystal, BSE suggested homogeneous phase, but EBSD shows the growth direction is along ***c*** in principle, but with slight different orientations. Region 1 and 2 are pseudosymmetry, along ***c*** and –***c***, respectively. Region 4 shows biggest variation, which is 3° tilt away from the ***c*** axis.

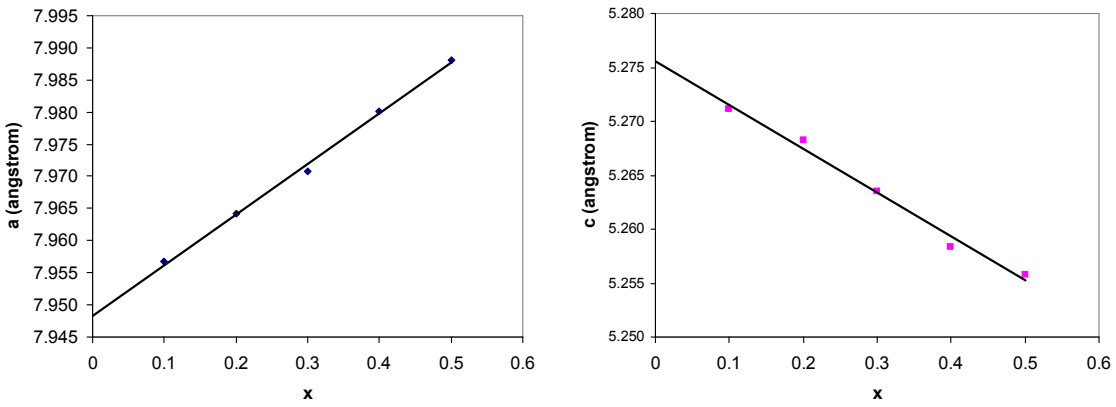

Figure S7. Lattice parameters variation with x for $[La_{1+x}Ca_{1-x}]_2[Ga]_2[Ga_2O_{7+x/2}]_2$..

Table S1.PXRD Refinement details

Structure x=0

Phase name	Structure
R-Bragg	5.173
Spacegroup	P-421m
Scale	0.0002939(13)
Cell Mass	1000.293
Cell Volume (Å^3)	333.7584(43)
Wt% - Rietveld	100.000
Crystallite Size	
Cry Size Lorentzian (nm)	488(39)
Cry Size Gaussian (nm)	10000(49000)
Strain	
Strain L	0.0237(49)
Strain G	0.00(25)

Crystal Linear Absorption Coeff. (1/cm)	693.2323(89)
Crystal Density (g/cm^3)	4.976734(64)
Preferred Orientation (Dir 1 : 312)	1.1532(54)
PV_TCHZ peak type	
U	0.00102(37)
V	-0.00071(27)
W	0.000111(52)
Z	0
X	0.0001(21)
Y	0
Lattice parameters	
a (Å)	7.955984(43)
c (Å)	5.272838(37)

Site	Np	x	y	z	Atom	Occ	Beq
Ca1	4	0.33996(13)	0.16004(13)	0.50516(33)	Ca+2	0.5	0.545(32)
La1	4	0.33996(13)	0.16004(13)	0.50516(33)	La+3	0.5	0.545(32)
Ga1	2	0.00000	0.00000	0.00000	Ga+3	1	0.257(56)
Ga2	4	0.14447(17)	0.35553(17)	0.96421(36)	Ga+3	1	0.344(44)
O1	2	0.50000	0.00000	0.2045(24)	O-2	1	0.21(12)
O2	4	0.13605(90)	0.36395(90)	0.3053(14)	O-2	1	0.21(12)
O3	8	0.09056(81)	0.17056(86)	0.7905(12)	O-2	1	0.21(12)

Structure x=0.1

Phase name	Structure
R-Bragg	7.327
Spacegroup	P-421m
Scale	0.0003579(65)
Cell Mass	996.4(66)
Cell Volume (Å^3)	333.713(86)
Wt% - Rietveld	100.0000000000(19)
Crystallite Size	
Cry Size Lorentzian (nm)	107.6(72)
Cry Size Gaussian (nm)	10000(470000)
Strain	
Strain L	0.000(18)
Strain G	0.0(13)
Crystal Linear Absorption Coeff. (1/cm)	682(10)
Crystal Density (g/cm^3)	4.958(33)
Preferred Orientation (Dir 1 : 411)	1.235(12)
PV_TCHZ peak type	
U	0.0009(20)
V	-0.0011(24)
W	0.00032(65)
Z	0
X	0.0001(90)
Y	0
Lattice parameters	
a (Å)	7.95670(91)
c (Å)	5.27117(61)

Site	Np	x	y	z	Atom	Occ	Beq
La1	4	0.33905(30)	0.16095(30)	0.50471(76)	La+3	0.486(17)	0.4(21)
					Ca+2	0.514(17)	0.4(70)
Ga1	2	0.00000	0.00000	0.00000	Ga+3	1	0.04(14)
Ga2	4	0.14454(38)	0.35546(38)	0.96641(82)	Ga+3	1	0.05(11)
O1	2	0.50000	0.00000	0.2074(53)	O-2	1	0.07(27)
O2	4	0.1446(21)	0.3554(21)	0.3218(30)	O-2	1	0.07(27)
O3	8	0.0898(19)	0.1600(23)	0.7990(26)	O-2	1	0.07(27)
O4	4	0.751(97)	0.251(97)	0.17(16)	O-2	0.025	1

Structure x=0.2

Phase name	Structure
R-Bragg	5.862
Spacegroup	P-421m
Scale	0.0003491(23)
Cell Mass	1043.024
Cell Volume (Å^3)	334.152(18)
Wt% - Rietveld	100.000
Crystallite Size	
Cry Size Lorentzian (nm)	146.0(54)
Crystal Linear Absorption Coeff. (1/cm)	775.408(43)
Crystal Density (g/cm^3)	5.18322(29)
Preferred Orientation (Dir 1 : 211)	1.131(12)
PV_TCHZ peak type	
U	0.0007(10)
V	-0.0011(15)
W	0.00036(50)
Z	0
X	0.0001(32)
Y	0
Lattice parameters	
a (Å)	7.96416(19)
c (Å)	5.26822(15)

Site	Np	x	y	z	Atom	Occ	Beq
La1	4	0.33956(30)	0.16044(30)	0.5091(10)	La+3	0.600(12)	1.000(61)
					Ca+2	0.4	1.000(61)
Ga1	2	0.00000	0.00000	0.00000	Ga+3	1	1.000(74)
Ga2	4	0.14401(43)	0.35599(43)	0.9703(12)	Ga+3	1	1.000(74)
O1	2	0.50000	0.00000	0.1811(61)	O-2	1	1.00(18)
O2	4	0.1497(25)	0.3503(25)	0.3042(37)	O-2	1	1.00(18)
O3	8	0.0923(22)	0.1455(25)	0.7980(32)	O-2	1	1.00(18)
O4	4	0.751(66)	0.251(66)	0.23(10)	O-2	0.05	1

Structure x=0.3

Phase name	Structure
R-Bragg	5.243
Spacegroup	P-421m
Scale	0.0002968(25)
Cell Mass	1056.142
Cell Volume (Å^3)	334.401(16)
Wt% - Rietveld	100.000
Crystallite Size	
Cry Size Lorentzian (nm)	131.5(60)
Strain	
Strain L	0.000(13)
Crystal Linear Absorption Coeff. (1/cm)	799.031(38)
Crystal Density (g/cm^3)	5.24449(25)
Preferred Orientation (Dir 1 : 211)	1.138(10)
PV_TCHZ peak type	
U	0.0028(15)
V	-0.0038(20)
W	0.00118(64)
Z	0
X	0.0001(69)
Y	0
Lattice parameters	
a (Å)	7.97074(16)
c (Å)	5.26346(13)

Site	Np	x	y	z	Atom	Occ	Beq
La1	4	0.33823(25)	0.16177(25)	0.50704(77)	La+3	0.6291	0.323(57)
					Ca+2	0.3709	0.323(57)
Ga1	2	0.00000	0.00000	0.00000	Ga+3	1	0.23(12)
Ga2	4	0.14230(35)	0.35770(35)	0.96657(89)	Ga+3	1	0.081(94)
O1	2	0.50000	0.00000	0.1913(59)	O-2	1	1
O2	4	0.1516(22)	0.3484(22)	0.3357(35)	O-2	1	1
O3	8	0.0934(20)	0.1532(23)	0.7953(31)	O-2	1	1
O4	4	0.710(29)	0.210(29)	0.267(55)	O-2	0.075	1

Structure x = 0.4

Phase name	Structure
R-Bragg	6.401
Spacegroup	P-421m
Scale	0.0002074(18)
Cell Mass	1085.755
Cell Volume (Å^3)	334.861(41)
Wt% - Rietveld	100.000
Crystallite Size	
Cry Size Lorentzian (nm)	96.8(52)
Crystal Linear Absorption Coeff. (1/cm)	856.58(10)
Crystal Density (g/cm^3)	5.38414(66)
Preferred Orientation (Dir 1 : 211)	1.112(14)
PV_TCHZ peak type	
U	0.0025(32)
V	-0.0042(47)
W	0.0016(17)
Z	0
X	0.0001(70)
Y	0
Lattice parameters	
a (Å)	7.98007(42)
c (Å)	5.25838(32)

Site	Np	x	y	z	Atom	Occ	Beq
La1	4	0.33953	0.16047	0.50571	La+3	0.7	1
					Ca+2	0.3	1
Ga1	2	0.00000	0.00000	0.00000	Ga+3	1	1
Ga2	4	0.14540	0.35460	0.97649	Ga+3	1	1
O1	2	0.50000	0.00000	0.21810	O-2	1	1
O2	4	0.16042	0.33958	0.32150	O-2	1	1
O3	8	0.09361	0.15359	0.77968	O-2	1	1
O4	4	0.74884	0.24884	0.23964	O-2	0.1	1

Structure x=0.5

Phase name	Structure
R-Bragg	4.010
Spacegroup	P-421m
Scale	0.00006741(35)
Cell Mass	1051.866
Cell Volume (Å^3)	335.363(13)
Wt% - Rietveld	100.000
Crystallite Size	
Cry Size Lorentzian (nm)	0(49000000000)
Strain	
Strain L	0.0661(64)
Crystal Linear Absorption Coeff. (1/cm)	781.317(31)
Crystal Density (g/cm^3)	5.20828(21)

Preferred Orientation (Dir 1 : 001)	1.2100(63)
PV_TCHZ peak type	
U	0.00020(52)
V	-0.00010(40)
W	0.000008(79)
Z	0
X	0.0001(34)
Y	0
Lattice parameters	
a (Å)	7.98804(14)
c (Å)	5.255759(98)

Site	Np	x	y	z	Atom	Occ	Beq
Ca1	4	0.33710	0.16290	0.50468	Ca+2	0.3898	0.831(35)
La1	4	0.33710	0.16290	0.50468	La+3	0.6102	0.831(35)
Ga1	2	0.00000	0.00000	0.00000	Ga+3	1	1.726(85)
Ga2	4	0.14276(23)	0.35724(23)	0.96533(53)	Ga+3	1	1.691(63)
O1	2	0.50000	0.00000	0.2050(27)	O-2	1	0.06(38)
O2	4	0.13156(94)	0.36844(94)	0.3203(17)	O-2	1	0.26(24)
O3	8	0.09680(93)	0.1640(10)	0.7951(14)	O-2	1	0.09(17)
O4	4	0.7025(88)	0.2025(88)	0.175(15)	O-2	0.125	0.8(25)

Table S2. Fitting parameters for single crystal $[NdCa]_2[Ga]_2[Ga_2O_7]_2$ along *c* axis.

Heating: R(RQ)(RQ)

T	R	R_{HF}	Y_{HF}	n_{HF}	C_{HF}	R_{LF}	Y_{LF}	n_{LF}	C_{LF}
ºC	Ohm ·cm²	Ohm ·cm²			F/cm²				F/cm²
600	172.8	5384	6.26E-09	0.9414	3.30E-09	16880	4.60E-05	0.6122	3.92E-05
650	173.9	3194	6.25E-09	0.9468	3.40E-09	5990	6.42E-05	0.627	3.64E-05
700	174.9	1389	4.39E-09	0.9834	3.59E-09	854.8	1.37E-04	0.6264	3.80E-05
750	165.1	721.7	4.02E-09	1	1	256.9	2.44E-04	0.6134	4.26E-05
800	151.9	388.7	4.95E-09	1	1	97.52	4.15E-04	0.6323	6.43E-05
850	137.8	222.7	6.64E-09	1	1	38.84	5.72E-04	0.6568	7.82E-05

Cooling: R(RQ)(RQ)

T	R	R_{HF}	Y_{HF}	n_{HF}	C_{HF}	R_{LF}	Y_{LF}	n_{LF}	C_{LF}
ºC	Ohm ·cm²	Ohm ·cm²			F/cm²	Ohm ·cm²			F/cm²
600	201	3897	3.15E-09	0.9923	2.89E-09	6652	6.40E-05	0.6394	3.95E-05
650	215.1	1952	3.15E-09	1	3.15E-09	1956	1.06E-04	0.6394	4.36E-05
700	184.6	1083	3.52E-09	1	3.52E-09	807	1.73E-04	0.6301	5.45E-05
750	164.5	628.7	4.07E-09	1	4.07E-09	344.1	2.88E-04	0.6111	6.62E-05
800	151.4	374.1	5.02E-09	1	5.02E-09	124.2	4.93E-04	0.5834	6.71E-05