SUPPORTING INFORMATION

Cation Substitutional Chemistry in the $R_xX_{12}Z$ -Type Structure for Four Lanthanum Iodide ExamplesPRIVILEGED DOCUMENT
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Table S1. Some crystallographic and refinement data for five $ALa_6L_{12}Os$ compounds^a

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Cation composition.	Na ₁	(Ca _{0.906} La _{0.094})	(Ca _{0.621} La _{0.379})	Sr ₁	(Sr _{0.526} La _{0.474})
<i>a</i> , <i>c</i> (Å)	16.165(2), 11.162(3)	16.098(3), 11.157(4)	16.118(2), 11.075(2)	16.083(2), 11.366(3)	16.106(2), 11.145(2)
<i>V</i> (Å ³)	2464(11)	2504(1)	2491.7(7)	2546.1(9)	2503.7(7)
<i>d</i> _{calc} (g/cm ³)	5.061	5.153	5.171	5.174	5.241
μ (Mo K α , mm ⁻¹)	22.167	22.562	22.641	23.654	23.960
Crystal dimensions (mm)	0.16 x 0.12 x 0.12	0.12 x 0.19 x 0.12	0.12 x 0.19 x 0.12	0.12 x 0.12 x 0.09	0.10 x 0.10 x 0.09
Octant measured	$\pm h, +k, +l$	$\pm h, +k, \pm l$	$\pm h, +k, \pm l$	$\pm h, \pm k, \pm l$	$\pm h, +k, \pm l$
No. measured reflections	1817	2712	3415	5077	3434
No. independent reflections, <i>R</i> (int) (<i>I</i> > 0)	1655, 0.0867	1293, 0.1128	1631, 0.1391	1641, 0.1353	1638, 0.1077
No. independent observed reflections (<i>I</i> $\geq$ 2 σ _{<i>I</i>})	839	858	725	930	827
No. of variables	33	34	34	33	34
Relative transmission factor range	0.3882–1.00	0.5155–1.00	0.7469–1.00	0.5528–1.00	0.2249–1.00
Extinction parameter	$0.6(2) \times 10^{-5}$	$12.6(4) \times 10^{-5}$	$13.3(9) \times 10^{-5}$	$0.01(5) \times 10^{-5}$	$1.1(2) \times 10^{-4}$
Goodness of fit	0.983	0.969	0.923	1.003	0.955
<i>R</i> ₁ , <i>wR</i> ₂ (<i>I</i> $\geq$ 2 σ _{<i>I</i>})	0.0567, 0.1445	0.0372, 0.0660	0.0534, 0.0849	0.0509, 0.0840	0.0580, 0.1182
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.1566, 0.1892	0.0826, 0.0782	0.1761, 0.1117	0.1283, 0.1029	0.1536, 0.1499
Largest residual peaks (e/Å ³)	3.04 (0.8 Å from Os), -3.20 (0.8 Å from Os)	1.29 (0.8 Å from I2), -1.91 (0 Å from Os)	2.53 (1.7 Å from La1), -3.73 (0 Å from Os)	1.81 (0.8 Å from I2), -1.55 (1.0 Å from Sr)	3.28 (1.29 Å from Os), -3.14 (1.06 Å from La1)

Table S1 (cont)

^a Common parameters: Space group *R*-3 (no.148), *Z* = 3; Rigaku AFC4 diffractometer, Mo K α radiation, 2θ - ω scans, $2\theta_{\text{max}}$ = 60°.

Table S2. Structural Parameters for five refined $A_xLa_{1-x}(La_6I_{12}Os)$ phasesPositional and thermal parameters for $Na_1La_6I_{12}Os$

Atom	x	y	z	Ueq	Occ.	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
La1	0.95539(7)	0.83858(1)	0.1499(1)	0.0260(3)	1	0.0259(6)	0.0280(5)	0.0234(6)	-0.0057(5)	-0.0008(5)	0.0128(4)
I1	0.86922(9)	0.94953(8)	0.3340(1)	0.0311(3)	1	0.0344(6)	0.0326(6)	0.0249(7)	0.0035(6)	-0.0064(5)	0.0156(5)
I2	0.31272(9)	0.0790(1)	0.0024(2)	0.0372(4)	1	0.0231(6)	0.0494(8)	0.0377(9)	-0.0171(6)	-0.0063(6)	0.0172(5)
Os	0	0	0	0.0152(4)	1	0.0169(4)	U ₁₁	0.0120(8)	0	0	1/2 U ₁₁
Na	0	0	1/2	0.052(6)	1	0.062(9)	U ₁₁	0.03(1)	0	0	1/2 U ₁₁

Positional and thermal parameters for $(Ca_{0.906}La_{0.094})La_6I_{12}Os$

Atom	x	y	z	Ueq	Occ.	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
La1	0.95444(5)	0.88236(5)	0.14793(9)	0.0139(3)	1	0.0197(4)	0.0210(4)	0.0237(5)	0.0035(3)	-0.0007(3)	0.0091(4)
I1	0.82040(6)	0.94942(6)	0.3400(1)	0.0251(3)	1	0.0257(5)	0.0260(5)	0.0242(7)	0.0020(4)	0.0056(4)	0.0133(4)
I2	0.76380(7)	0.07725(8)	0.0027(1)	0.0373(4)	1	0.0351(6)	0.0488(7)	0.043(1)	-0.0208(5)	-0.0135(5)	0.0322(5)
Os	0	0	0	0.0139(3)	1	0.0134(4)	U ₁₁	0.0150(7)	0	0	1/2 U ₁₁
Ca	0	0	1/2	0.034(2)	0.906(1)	0.034(3)	U ₁₁	0.034(4)	0	0	1/2 U ₁₁
La2	0	0	1/2	0.034	0.094(1)	0.034	U ₁₁	0.034	0	0	1/2 U ₁₁

Table S2 (cont.)

Positional and thermal parameters for $(\text{Ca}_{0.621}\text{La}_{0.379})\text{La}_6\text{I}_{12}\text{Os}$

Atom	x	y	z	Ueq	Occ.	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
La1	0.83736(8)	0.88290(7)	-0.1493(1)	0.0135(5)	1	0.0254(6)	0.0235(6)	0.0241(5)	0.0019(5)	0.0038(5)	0.0135(5)
I1	0.86881(9)	0.05145(9)	-0.3409(1)	0.0299(3)	1	0.0307(7)	0.0318(7)	0.0250(5)	0.0023(6)	-0.0034(6)	0.0141(6)
I2	0.6872(1)	0.9225(1)	-0.0019(1)	0.0390(4)	1	0.0219(6)	0.0532(9)	0.0409(8)	-0.0212(7)	-0.0074(6)	0.0189(6)
Os	0	0	0	0.0150(4)	1	0.0151(5)	U ₁₁	0.0150(9)	0	0	1/2 U ₁₁
Ca	0	0	1/2	0.044(5)	0.621(2)	0.028(2)	U ₁₁	0.076(6)	0	0	1/2 U ₁₁
La2	0	0	1/2	0.044	0.379(2)	0.028	U ₁₁	0.076	0	0	1/2 U ₁₁

Positional and thermal parameters for $\text{Sr}_1\text{La}_6\text{I}_{12}\text{Os}$

Atom	x	y	z	Ueq	Occ.	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
La1	0.88132(6)	0.83636(6)	0.14542(7)	0.0239(2)	1	0.0241(4)	0.0254(4)	0.0242(4)	-0.0053(4)	-0.0045(4)	0.0139(4)
I1	0.20135(6)	0.48382(6)	0.33538(8)	0.0266(2)	1	0.0266(5)	0.0267(5)	0.0265(4)	-0.0062(4)	-0.0040(4)	0.0134(4)
I2	0.07933(9)	0.31463(7)	-0.00252(9)	0.0359(3)	1	0.0477(6)	0.0206(4)	0.0392(6)	0.0074(4)	0.0193(5)	0.0169(4)
Os	0	0	0	0.0143(3)	1	0.0139(4)	U ₁₁	0.0153(6)	0	0	1/2 U ₁₁
Sr	0	0	1/2	0.0332(8)	1	0.040(1)	U ₁₁	0.020(2)	0	0	1/2 U ₁₁

Table S2 (cont. 2)

Positional and thermal parameters for (Sr_{0.526}La_{0.474})La₆I₁₂Os

Atom	x	y	z	Ueq	Occ.	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
La1	0.50386(9)	0.21577(8)	0.1850(1)	0.0231(3)	1	0.0197(6)	0.0216(6)	0.0290(5)	0.0024(4)	0.0029(4)	0.0111(5)
I1	0.61473(9)	0.14800(9)	-0.0040(1)	0.0276(3)	1	0.0233(7)	0.0284(8)	0.0309(5)	-0.0053(5)	-0.0017(4)	0.0128(6)
I2	0.4319(1)	0.0198(1)	0.3352(1)	0.0338(4)	1	0.0312(8)	0.0169(6)	0.0407(7)	0.0059(5)	-0.0108(5)	0.0025(6)
Os	0	0	0	0.0136(4)	1	0.0111(5)	U ₁₁	0.0186(7)	0	0	½ U ₁₁
Sr	0	0	1/2	0.044(2)	0.526(2)	0.026(2)	U ₁₁	0.080(3)	0	0	½ U ₁₁
La2	0	0	1/2	0.044	0.474(2)	0.026	U ₁₁	0.080	0	0	½ U ₁₁

Table S3. Selected angles for $(A_x\text{La}_{1-x})\text{La}_6\text{I}_{12}\text{Os}$ (deg.)

Crystal	$\text{NaLa}_6\text{I}_{12}\text{Os}$	$(\text{Ca}_{0.906}\text{La}_{0.094})\text{La}_6\text{I}_{12}\text{Os}$	$(\text{Ca}_{0.621}\text{La}_{0.379})\text{La}_6\text{I}_{12}\text{Os}$	$\text{SrLa}_6\text{I}_{12}\text{Os}$	$(\text{Sr}_{0.526}\text{La}_{0.474})\text{La}_6\text{I}_{12}\text{Os}$
La1–Os–La1	180.00(4)	180.00(4)	180.00(4)	180.00(4)	180.00(4)
La1–Os–La1	90.32(4)	90.24(2)	90.07(3)	90.31(2)	90.01(3)
La1–Os–La1	89.68(3)	89.76(2)	89.93(3)	89.69(2)	89.90(3)
I1–A/La2–I1	180.00(3)	180.00(3)	180.00(3)	180.00(3)	180.00(3)
I1–A/La2–I1	89.83(4)	88.11(2)	88.00(4)	88.83(2)	88.52(3)
I1–A/La2–I1	90.17(4)	90.89(2)	92.00(4)	91.17(2)	91.48(3)
Na–I1–La1	89.88(4)	91.06(2)	89.54(4)	91.35(3)	89.16(4)
Na–I1–La1	89.75(4)	90.90(2)	89.43(4)	91.13(3)	89.02(4)
La1–I1–La1	77.73(5)	76.84(3)	76.47(4)	77.05(3)	76.34(5)
La1–I2–La1	77.51(6)	77.56(4)	77.59(6)	77.69(4)	77.61(6)
La1–I2–La1	173.64(5)	172.51(3)	172.86(6)	172.10(4)	172.84(6)
Ia1–I2–La1	96.13(5)	94.95(3)	95.28(5)	94.54(4)	95.25(5)

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Figure S1. Resistivity of $\text{NaLa}_6\text{I}_{12}\text{Os}$. $\rho_{298} = 144 \mu\Omega\text{-cm}$, slope $-0.52(2) \mu\Omega\text{-cm K}^{-1}$.

Fig 3

Figure S2. Molar magnetic susceptibility data for $\text{SrLa}_6\text{I}_{12}\text{Os}$ and $\text{CaLa}_6\text{I}_{12}\text{Os}$.