Iridium Containing Honeycomb Delafossites by Topotactic Cation Exchange

Supplemental Material

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Supplemental Table S1: Crystallographic data for $Cu_3LiIr_2O_6$ at 295 K. Space group C2/c, *a* = 5.2910(2), *b* = 9.1434(5), *c* = 11.6203(5), beta = 98.798(8), 555.55(4) $Å^3$. Parameters = 27. Powder X-ray diffraction: λ = CuKα, 5-110 º2θ, data points = 5245, reflections = 401. Agreement factors: Rbragg = 19.6, Rf = 13.7, χ^2 = 3.87.

Atom	Position	*x*	*y*	*z*	*B*	*Occ*
Cu1	4e	0	0.728(3)	¼	1.5	1
Cu2	4e	0	0.454(3)	¼	1.5	1
Cu3	4e	½	0.581(3)	¼	1.5	1
Ir1	8f	0.238(1)	0.078(1)	0.003(1)	0.5	0.79(1)
Li1	8f	0.238(1)	0.078(1)	0.003(1)	0.5	0.21(1)
Ir2	4d	¼	¾	0	0.5	0.57(1)
Li2	4d	¼	¾	0	0.5	0.43(1)
O1	8f	0.44(1)	0.224(7)	0.084(3)	0.93	1
O2	8f	1.01(1)	0.487(5)	0.100(5)	0.93	1
O3	9f	0.45(1)	0.566(7)	0.091(4)	0.93	1

Supplemental Table S2: Crystallographic data for $Cu_3NaIr_2O_6$, 295 K. Space group C2/m, *a* = 5.39017(19), *b* = 9.29984(36), *c* = 5.97093(20), beta = 107.6399(36), 285.24(2) $Å^3$. Parameters = 23. Powder X-ray diffraction: λ = CuKα, 5-110 º2θ, data points = 5251, reflections = 238, parameters. Agreement factors: R_{Bragg} = 8.50 R_f = 7.27. Powder neutron diffraction: λ = 1.5398, 13-156 º2θ, data points = 3296, reflections = 342. Agreement factors: R_{Bragg} = 10.8 R_f = 8.71. Global χ^2 = 1.42.

Atom	Position	*x*	*y*	*z*	*B*	*Occ*
Cu1	2c	0	0	½	1.9(1)	1
Cu2	4h	0	0.340(2)	½	1.9(1)	1
Ir1	4g	0	0.160(1)	0	0.54(1)	0.57(3)
Na1	4g	0	0.160(1)	0	0.54(1)	0.43(3)
Ir2	2b	0	½	0	0.54(1)	0.85(3)
Na2	2b	0	½	0	0.54(1)	0.15(3)
O1	8j	0.881(2)	0.343(2)	0.172(2)	0.8(1)	1
O2	4i	0.916(3)	0	0.183(4)	0.8(1)	1

Table S3: Crystallographic data for $Cu_3NaIr_2O_6$ at 5 K. Space group C2/c, *a* = 5.3882(1), *b* = 9.2908(2), *c* = 11.5196(2), beta = 99.050(3), 569.50(2) Å^3. *Bov* = -0.52(1), parameters = 21. Powder neutron diffraction: λ = 1.5406, 13-156 º2θ, data points = 3296, reflections = 642. Agreement factors: Rbragg = 9.15, Rf = 7.75, χ^2 = 2.37. **B* and *Occ* are fixed to the values obtained for the refinement at RT, a universal B factor (*Bov*) is used to compensate for changes in thermal parameters.

Atom	Position	*x*	*y*	*z*	*B**	*Occ**
Cu1	4e	0	0.757(2)	¼	1.5	1
Cu2	4e	0	0.421(2)	¼	1.5	1
Cu3	4e	½	0.593(1)	¼	1.5	1
Ir1	8f	0.254(2)	0.080(1)	0.004(1)	0.51	0.76
Na1	8f	0.254(2)	0.080(1)	0.004(1)	0.51	0.24
Ir2	4d	¼	¾	0	0.51	0.52
Na2	4d	¼	¾	0	0.51	0.48
O1	8f	0.440(3)	0.237(2)	0.088(1)	0.93	1
O2	8f	0.941(3)	0.422(2)	0.080(1)	0.93	1
O3	9f	0.462(3)	0.576(2)	0.095(1)	0.93	1

Table S4: Unit cell refinements in C2/m of $Cu_3NaIr_2O_6$ and $Cu_3Li_2IrO_6$ as well as Na_2IrO_3 and Li_2IrO_3. Interlayer spacing and Ir-Ir distances are also given. All units in Å, unless otherwise noted.

Phase	Instrument	temp	Space group	a	b	c	beta	layer spacing	Ir-Ir dis	ref
Na_2IrO_3	SXRD	RT	C2/m	5.4270(1)	9.395(1)	5.614(1)	109.037(18)	5.307(1)	3.130(7) 3.138(14)	1
$Cu_3NaIr_2O_6$	NPD + PXRD	RT	C2/m	5.3902(2)	9.2998(4)	5.9709(2)	108.640 (4)	5.6902(2)	3.080(5) 3.159(11)	this work
$Cu_3NaIr_2O_6$	NPD	5 K	C2/m	5.3759(2)	9.3136(3)	5.9720(1)	107.757(2)	5.6875(1)	3.097(4) 3.118(6)	this work
Li_2IrO_3	PXRD	RT	C2/m	5.1633(2)	8.9290(3)	5.1219(2)	109.759(3)	4.8203(1)	2.973(3) 2.979(1)	O'Mally
$Cu_3LiIr_2O_6$	PXRD	RT	C2/m	5.2908(3)	9.1463(5)	6.0114(2)	107.198(5)	5.7426(2)	3.041(4) 3.078(6)	this work

Table S5: Bond lengths and angles of $Cu_3NaIr_2O_6$ (s.g. = C2/m) at room temperature and 5 K

Phase	**radiation**	**temp**	**Ir-Ir dis " Ir-Ir mean, STD, % dev**	**Ir-O1 Ir-O2 Ir-O avg, STD, % dev**	**Na-O1 Na-O2 Na-O avg, STD, % dev**	**Ir-O1-Ir Ir-O2-Ir Ir-O-Ir avg**
$Cu_3NaIr_2O_6$	Neutron +X-ray	RT	3.080(5) 3.159(11) **3.12** +/- 0.06, 1.8%	1.999(9), 2.181(15) 1.980(13) **2.053** +/- 0.11, 5.3%	2.001(12) 2.176(13) **2.089** +/- 0.12, 5.7%	97.7(4) 98.5(3) **98.1**
$Cu_3NaIr_2O_6$	Neutron	5 K	3.097(4) 3.118(6) **3.108** +/- 0.15, 4.8%	2.016(6), 2.154(8) 2.046(8) **2.072** +/- 0.073, 3.5%	1.946(6) 2.157(8) **2.052** +/- 0.15, 7.3%	96.71(15) 97.5(3) **97.1**

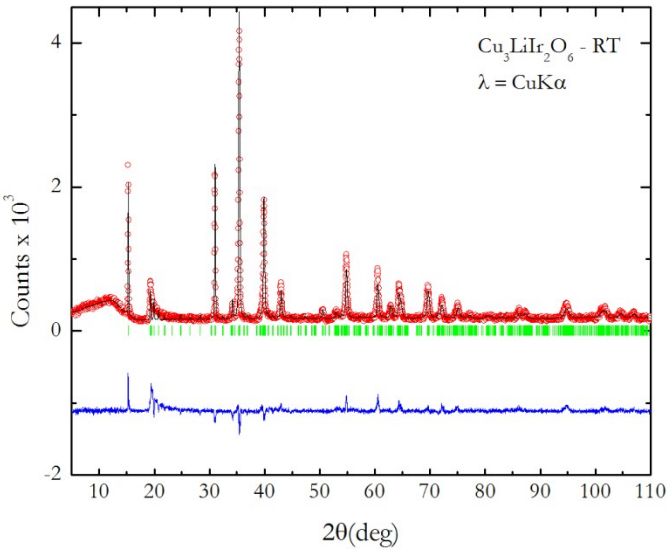

Figure S1: Powder X-ray diffraction pattern and Rietveld fit of $Cu_3LiIr_2O_6$ at room temperature in space group C2/c. Data is given as red circles, the fit as a black line, the difference as a blue line and Bragg reflections as green hashes.

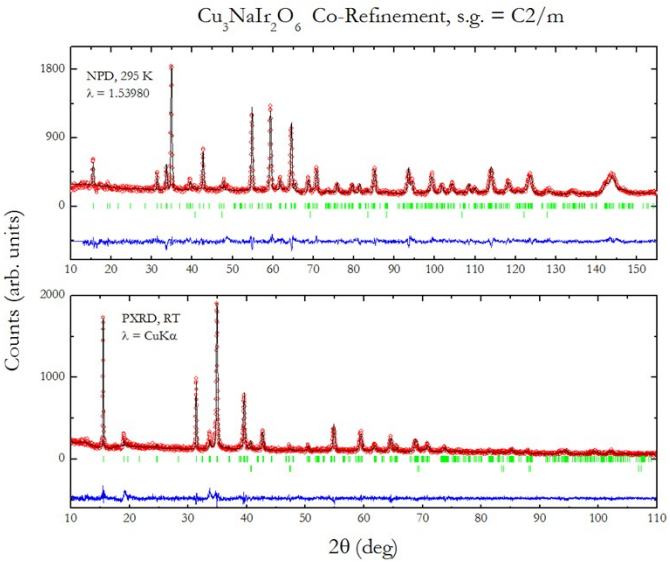

Figure S2: Neutron (upper panel) and X-ray (lower panel) powder diffraction of $Cu_3NaIr_2O_6$ (s.g. = C2/m) at 295 K with Rietveld fit. Data is given as red circles, the fit as a black line, the difference as a blue line and Bragg reflections as green hashes.

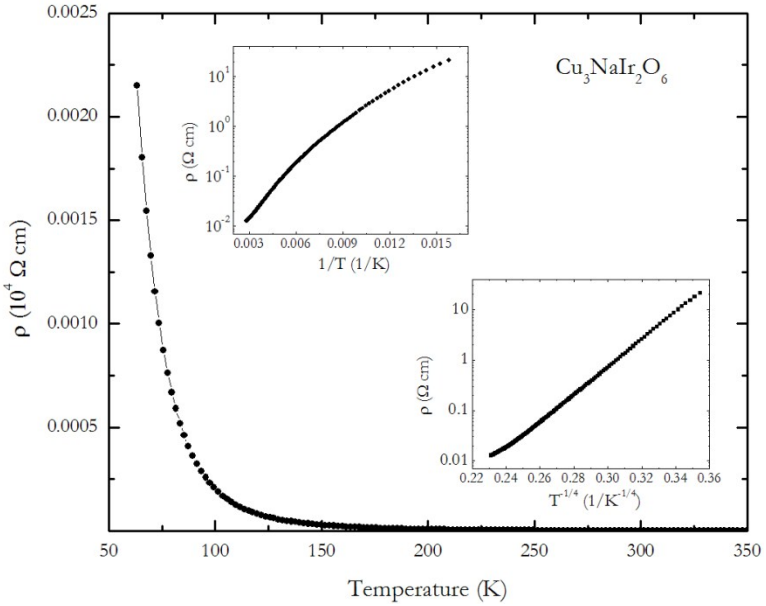

Figure S3: Resistivity ρ (Ω•cm), of $Cu_3NaIr_2O_6$ from 350 to 65 K measured upon cooling. Upper left inset - log plot of ρ vs. 1/T. The date cannot be fitted to an activated Arrhenius behavior $\rho(T) = \exp(-\Delta/T)$. Lower right inset - log plot of ρ vs. $1/T^{-1/4}$ allowing for a good fit to an activated $\rho(T) = \exp[(-\Delta/T)^{1/4}]$ associated with a variable-range hopping mechanism and similar to Na_2IrO_3.{Singh, 2010 #930}

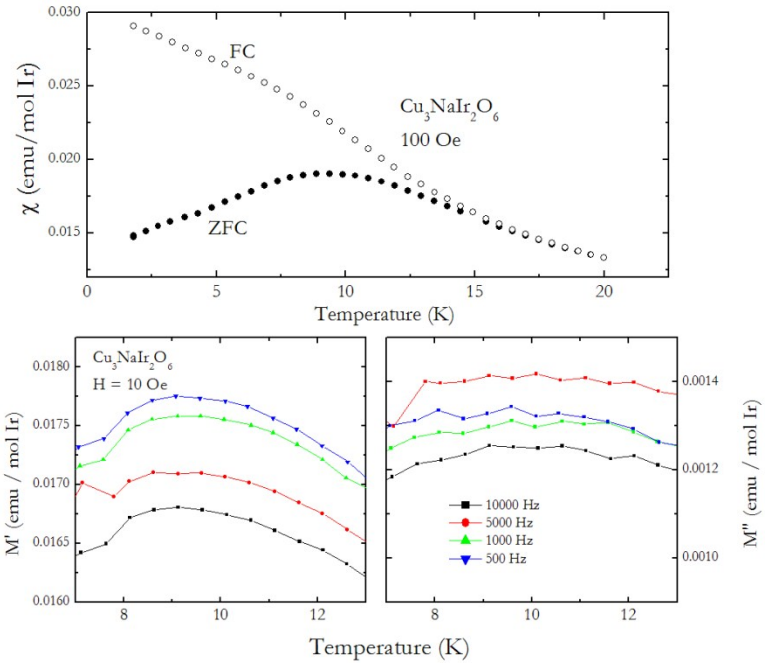

Figure S4: Upper – Field cooled (FC) and zero-field cooled (ZFC) magnetization of $Cu_3NaIr_2O_6$ measured with an applied field of 100 Oe. Lower – AC magnetization, real M' (Left) and imaginary (right) portions of the signal in the temperature range of the magnetic transition. Samples were measured with a 10 Oe applied field and 500, 1000, 5000 and 10,000 Hz. A change in the transition temperature with frequency, a classic characteristic of a spin-glass, is not observed.

1. Choi, S. K.; Coldea, R.; Kolmogorov, A. N.; Lancaster, T.; Mazin, I. I.; Blundell, S. J.; Radaelli, P. G.; Singh, Y.; Gegenwart, P.; Choi, K. R.; Cheong, S. W.; Baker, P. J.; Stock, C.; Taylor, J., Spin waves and revised crystal structure of honeycomb iridate Na2IrO3. *Phys Rev Lett* **2012,** 108, (12), 127204.