New Honeycomb Iridium (V) Oxides: $NaIrO_3$ and $Sr_3CaIr_2O_9$. Supplementary Information

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1 Synthesis of $NaIrO_3$

Polycrystalline Na_2IrO_3 was prepared *via* previously reported methods[1]. To prepare $NaIrO_3$, Polycrystalline Na_2IrO_3 was removed from the glovebox and immediately combined on the benchtop with a stock solution of elemental Bromine (Sigma–Aldrich, 99.99%) in acetonitrile (Fischer Scientific, HPLC grade). The progress of the reaction was monitored visually by observing a disappearance of color the from oxidant solution, and was presumed to be complete when the color reached a steady state or disappeared completely, depending on the targeted product stoichiometry. Upon reaching completion, the fine, black, polycrystalline product was collected *via* vacuum filtration and rinsed several times with fresh acetonitrile to remove crystalline NaBr.

2 Synthesis of $Sr_3CaIr_2O_9$

Polycrystalline $Sr_3CaIr_2O_9$ was prepared *via* conventional solid state synthesis: $SrCO_3$ (NOAH Technologies, 99.9%), $CaCO_3$ (NOAH Technologies, 99.98%) and IrO_2 (J&J Materials, 99%) were ground thoroughly in an agate mortar and pestle, heated in a capped alumina crucible to 750°C at 200°C/hr, held at temperature for 12 hours, and then furnace-cooled to room temperature. The powder was then reground and pelletized, heated to 1050°C at 200°C/hr in the same uncapped crucible, held at temperature for 80 hours, and then furnace-cooled to room temperature.

3 Characterization

All laboratory X-ray powder diffraction (XRPD) data were collected on a Bruker D8 Focus diffractometer with a LynxEye CCD detector. Neutron Powder Diffraction (NPD) data were collected on the BT-1 powder diffractometer at the NIST Center for Neutron Research. Ge (311) ($\lambda = 2.077$ nm) monochromation along with 15' and 60' source and sample collimation were employed, and the sample was housed in a 4mm cylindrical vanadium can. A high-temperature vacuum furnace was used for both 300K and 1100K diffraction experiments. Synchrotron XRPD data were collected at Argonne National Laboratory *via* the Advanced Photon Source 11-BM rapid access mail-in program. DC magnetization measurements were collected on powder samples, and four-probe resistance measurements were performed on rectangular bars cut from sintered polycrystalline pellets. All physical properties measurements were performed on a Quantum Design Physical Property Measurement system.

References

[1] J. W. Krizan, J. H. Roudebush, G. M. Fox, & R. J. Cava, The chemical instability of Na_2IrO_3 in air, *Materials Research Bulletin*, **52**, 162-166 (2014)

$NaIrO_3$	($P\bar{1}$ (2))	T = RT			
a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
5.2808(3)	5.2870(3)	6.0014(3)	90.002(9)	115.762(6)	60.112(5)
	Atom	Wyckoff Site	x, y, z	occ.	100×U_{iso}
	Ir1	(2i)	0.1641(5), 0.1562(6), 0.0098(2)	1	0.16(2)
	Na1	(1e)	$\frac{1}{2}$, 0, $\frac{1}{2}$	1	0.47(9)
	Na2	(2i)	0.210(4), 0.663(4), 0.563(2)	0.5(1)	0.47(9)
	O1	(2i)	0.948(2), 0.468(2), 0.153(2)	1	1.1(1)
	O2	(2i)	0.239(2), 0.844(2), 0.206(3)	1	1.1(1)
	O3	(2i)	0.639(3), 0.103(3), 0.190(2)	1	1.1(1)
				χ^2	3.70
				R_{wp}	10.65
				R_p	8.00

Table 1: Structural parameters for $NaIrO_3$ obtained from Rietveld refinement to laboratory XRPD data.

$Sr_3CaIr_2O_9$	($P2_1/c$ (14))	T = 300 K		
a (Å)	b (Å)	c (Å)	β (°)	Volume (Å^3)
17.1476(9)	5.7126(3)	9.8841(6)	125.137(3)	791.7
Atom	Wyckoff Site	x, y, z	occ.	100×U_{iso}
Sr1	(4e)	0.254(2), 0.536(2), 0.750(2)	1	1.83(7)
Sr2	(4e)	0.417(1), 0.026(3), 0.080(2)	1	1.83(7)
Sr3	(4e)	0.921(1), 0.524(3), 0.089(2)	1	1.83(7)
Ca1	(2a)	0, $\frac{1}{2}$, $\frac{1}{2}$	1	1.28(3)
Ca2	(2d)	$\frac{1}{2}$, 0, $\frac{1}{2}$	1	1.28(3)
Ir1	(4e)	0.167(1), 0.995(3), 0.836(1)	1	1.25(8)
Ir2	(4e)	0.326(1), 0.499(3), 0.158(2)	1	1.25(8)
O1	(4e)	0.434(1), 0.027(3), 0.622(3)	1	1.64(5)
O2	(4e)	0.882(1), 0.995(4), 0.040(3)	1	1.64(5)
O3	(4e)	0.091(1), 0.734(4), 0.713(3)	1	1.64(5)
O4	(4e)	0.068(1), 0.288(4), 0.178(2)	1	1.64(5)
O5	(4e)	0.412(1), 0.814(4), 0.848(3)	1	1.64(5)
O6	(4e)	0.749(1), 0.793(5), 0.534(2)	1	1.64(5)
O7	(4e)	0.723(1), 0.212(4), 0.988(3)	1	1.64(5)
O8	(4e)	0.383(1), 0.220(4), 0.305(3)	1	1.64(5)
O9	(4e)	0.232(1), 0.501(4), 0.205(3)	1	1.64(5)
			χ^2	1.77
			R_{wp}	5.58
			R_p	4.12

Table 2: Structural parameters for $Sr_3CaIr_2O_9$ obtained from Rietveld refinement to Rietveld refinement to NPD and laboratory XRPD data.