_3R_ - like Polytypes of the Layered Honeycomb Delafossites with Optical Brilliance in the Visible

Supporting Information

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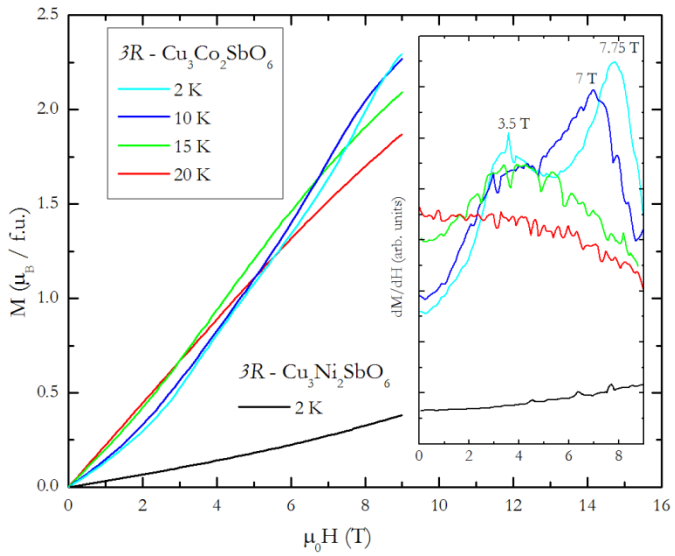

Figure S1) Magnetization of *3R* samples at various temperatures. The inset shows the change in magnetization with applied field (dM/dH) for comparison with other honeycomb Delafossite materials such as $Na_3Ni_2BiO_6$[1]

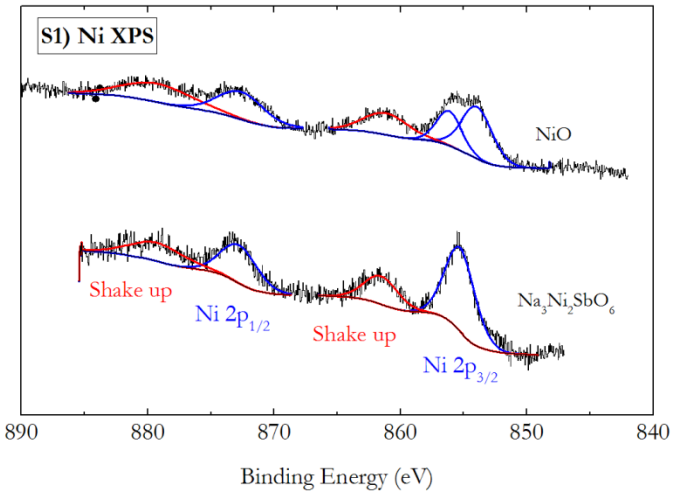

Figure S2) Ni XPS of NiO and $Na_3Ni_2SbO_6$

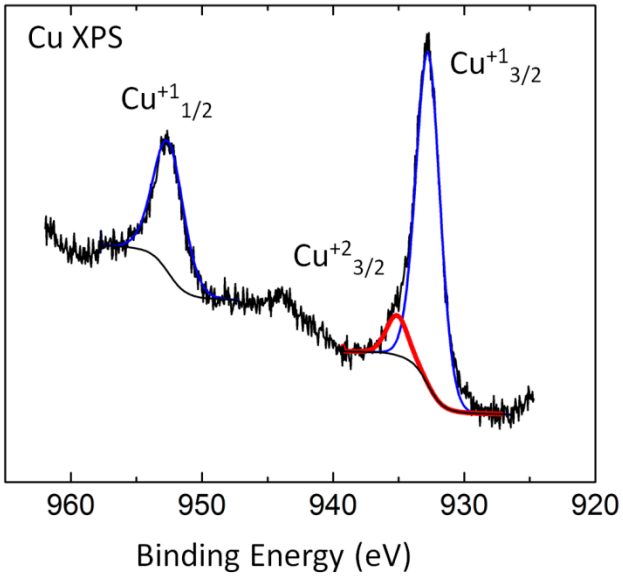

Figure S3) XPS Spectra of Cu peaks in the *3R* O_2 TGA sample.

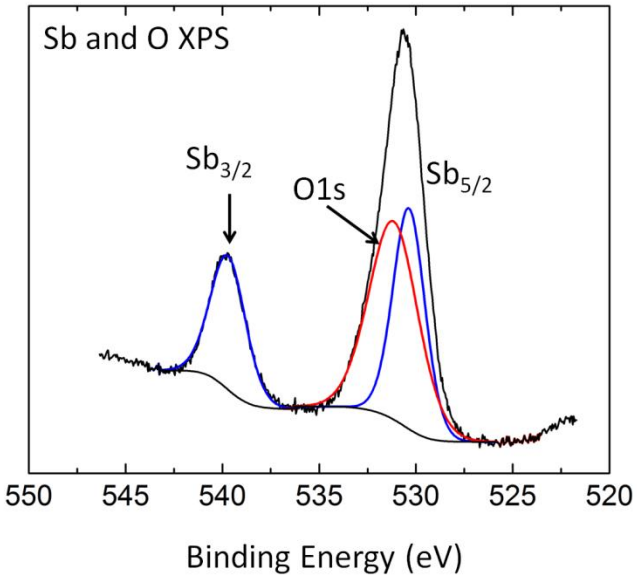

Figure S4) XPS Spectra of Sb/O peaks in the *3R* O_2 TGA sample.

Table S1: Heat treatment and peak area ratios extracted from XPS fits.

	Synthetic Heat Treatment	Cu^{2+} / Cu^{1+}	O^{2-} / Sb^{5+}
3R	400 ºC, vacuum, 24 h	Na	1
2H	1345 ºC, air, 24 h	0.2	2.5
3R O2 TGA	RT - 900 ºC - RT, O_2, 3 h	*0.1*	1.4

Further Discussion on XPS spectra

XPS of the *3R* sample heated in oxygen to 900 ºC reveals a new peak at 935 eV corresponding to the presence of Cu^{2+} (Figure S3). Further evidence for oxygen intercalation was found by measuring the and the peak areas Cu, O and Sb peak areas of each sample and comparing their ratios (Table S1). The heat treatment of the *2H* sample (1345 ºC, 24 hours) reaches the hottest temperature for the longest duration, it also has the largest Cu^{2+} / Cu^{1+} and O^{2-} /Sb^{5+} ratios which indicate that it has the largest O^{2-} uptake of the samples. The relative exposure of the *3R* O2 TGA sample to heat and O^{2-} was far less and therefore these ratios are smaller in this sample. We conclude that the higher heating temperature of the *2H* sample causes a larger lattice parameter expansion which allows for greater oxygen intercalation to the sample. Oxygen intercalation is further supported by the longer soaking time at high temperature. Combined, this

data suggests that oxygen intercalation is a sensitive kinetic process which could be tuned by adjusting temperature and soak time.

1. Seibel, E. M.; Roudebush, J. H.; Wu, H.; Huang, Q.; Ali, M. N.; Ji, H.; Cava, R. J., *Inorganic Chemistry* **2013,** *52,* 13605-13611.