

Supporting Information

The Hibonite Blue: A New Class of Intense Inorganic Blue Colorants

Brett A. Duell, Jun Li, M. A. Subramanian*

Department of Chemistry, Oregon State University, Corvallis, OR 97331

L*a*b* Color Space

Visible diffuse reflectance measurements were converted to CIEL*a*b* color space coordinates using a Konica Minolta CM-700d Spectrophotometer and the SpectraMagic NX program. The L*, or brightness coordinate is measured against black and white calibration standards, while the a* and b* values are converted directly from the diffuse reflectance spectrum. The a* value is measure of the “greenness” to “redness” of a material from negative to positive values, respectively. Likewise, the b* value is a measure of the “blueness” to “yellowness” of a material. This is shown in SI figure 1.

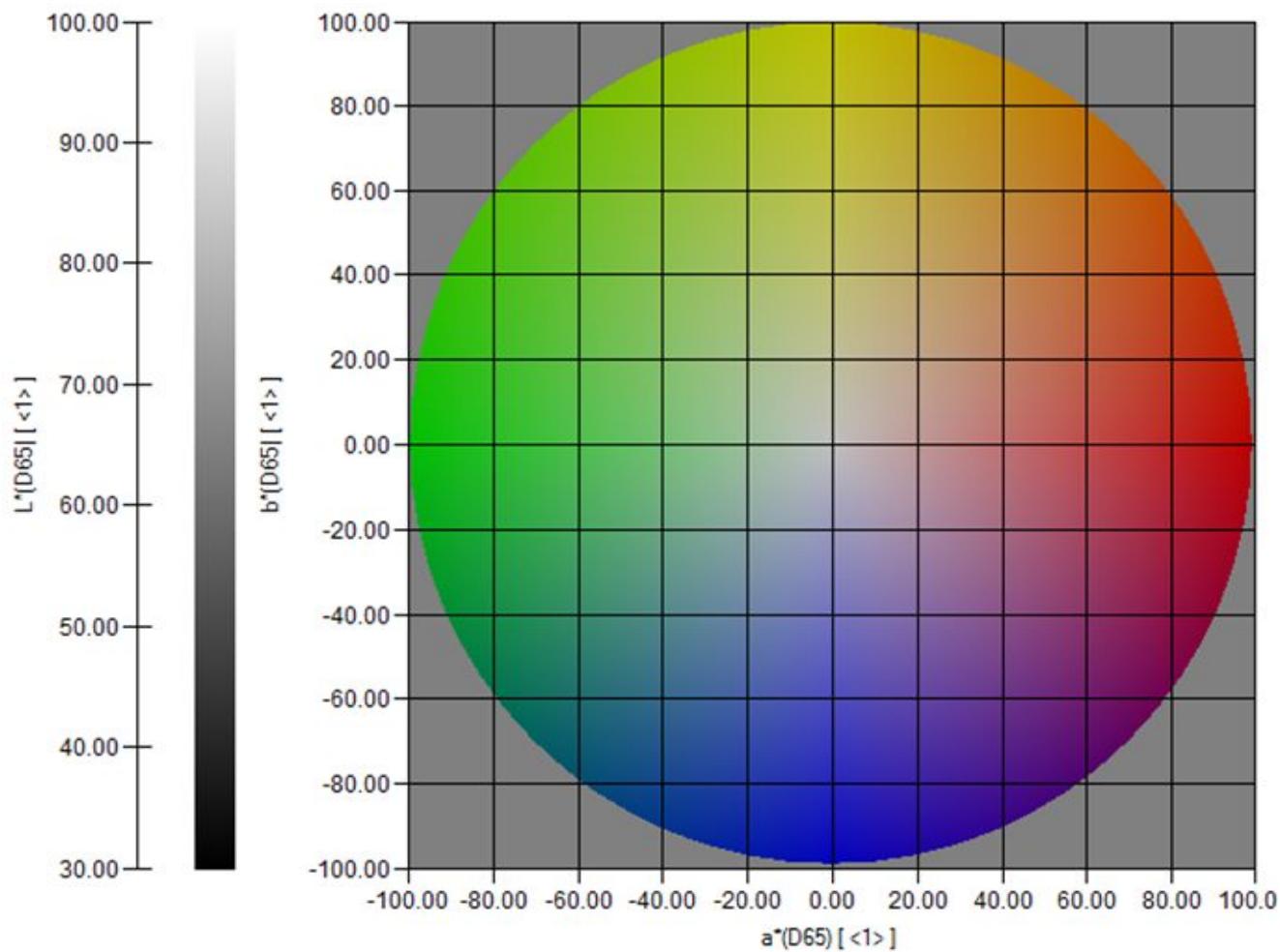


Figure S1. CIEL*a*b* coordinate space.

Determination of cobalt oxidation state

The magnetic susceptibility of $\text{CaAl}_{11}\text{Co}_{0.5}\text{Ti}_{0.5}\text{O}_{19}$ and $\text{CaAl}_{10}\text{CoTiO}_{19}$ was measured using a Quantum Design Model 6000 Physical Properties Measurement System in a constant 0.5 T field from 5 – 300 K (SI fig. 2(a)). The data was then fit to the Curie-Weiss Law in the region of 150 – 300 K. The resultant magnetic moments are higher than the expected spin-only values for a high-spin d^7 electron configuration. However, Co^{2+} commonly has much higher measured magnetic moments due to $L+S$ coupling resulting in moments ranging from 4.2 to 5.2 μ_B . The magnetic moments of $\text{CaAl}_{11}\text{Co}_{0.5}\text{Ti}_{0.5}\text{O}_{19}$ and $\text{CaAl}_{10}\text{CoTiO}_{19}$ fit within the framework of $L+S$ coupled high spin Co^{2+} .

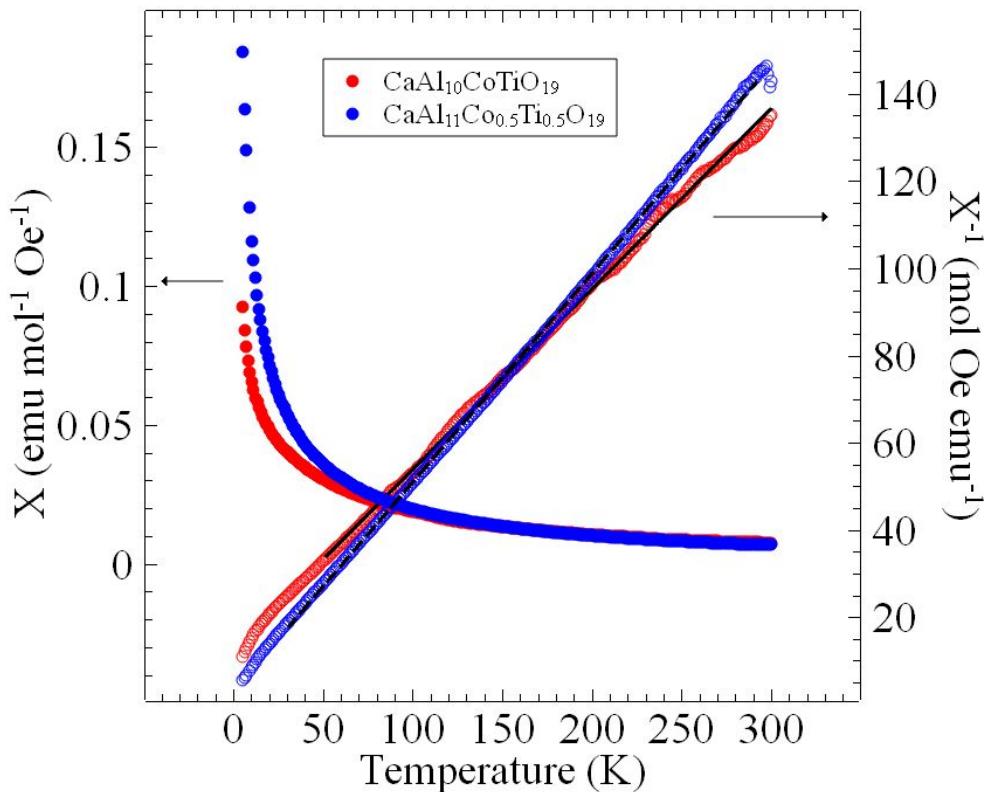


Figure S2. Magnetic susceptibility of $\text{CaAl}_{11}\text{Co}_{0.5}\text{Ti}_{0.5}\text{O}_{19}$ and $\text{CaAl}_{10}\text{CoTiO}_{19}$.

Table 1. Calculated magnetic moments of and theoretical spin-only magnetic moments for high spin Co^{2+}

Composition	Mag. Moment (th) (μ_B)	Mag. Moment (obs) (μ_B)
$\text{CaAl}_{10}\text{CoTiO}_{19}$	3.87	4.39
$\text{CaAl}_{11}\text{Co}_{0.5}\text{Ti}_{0.5}\text{O}_{19}$	3.87	4.09

Table S2. Rietveld refinement results of atomic sites of $\text{CaAl}_{10.6}\text{Co}_{0.7}\text{Ti}_{0.7}\text{O}_{19}$. Al³⁺ occupancies are not shown for clarity. All M sites have an occupancy of 1, except for $M2$, which has a total occupancy of 0.5.

Site	x	y	z	Occ.
Ca	1/3	2/3	3/4	1
$M1$ (Al ³⁺)	0	0	0	1
$M2$ (Al ³⁺)	0	0	0.2622(2)	0.370(6)
$M2$ (Co ²⁺)	0	0	0.2622(2)	0.084(1)
$M2$ (Ti ⁴⁺)	0	0	0.2622(2)	0.046(5)
$M3$ (Al ³⁺)	1/3	2/3	0.0268(2)	0.74(2)
$M3$ (Co ²⁺)	1/3	2/3	0.0268(2)	0.26(2)
$M4$ (Al ³⁺)	1/3	2/3	0.1886(2)	0.753(4)
$M4$ (Ti ⁴⁺)	1/3	2/3	0.1886(2)	0.247(4)
$M5$ (Al ³⁺)	0.1676(2)	0.3353(4)	0.89206(6)	0.981(2)
$M5$ (Ti ⁴⁺)	0.1676(2)	0.3353(4)	0.89206(6)	0.019(2)
$M5$ (Co ⁴⁺)	0.1676(2)	0.3353(4)	0.89206(6)	0
O1	0	0	0.1500(1)	1
O2	0.33333	0.66667	0.9427(1)	1
O3	0.1811(2)	0.3623(3)	1/4	1
O4	0.1528(1)	0.3055(2)	0.05312(4)	1
O5	0.5041(1)	0.0082(2)	0.15009(4)	1

Table S3. Rietveld refinement results of atomic sites of $\text{CaAl}_{10}\text{CoTiO}_{19}$. Al^{3+} occupancies are not shown for clarity. All M sites have an occupancy of 1, except for $M2$, which has a total occupancy of 0.5.

Site	x	y	z	Occ.
Ca	1/3	2/3	3/4	1
$M1$ (Al^{3+})	0	0	0	1
$M2$ (Al^{3+})	0	0	0.2629(3)	0.366(7)
$M2$ (Co^{2+})	0	0	0.2629(3)	0.087(3)
$M2$ (Ti^{4+})	0	0	0.2629(3)	0.042(6)
$M3$ (Al^{3+})	1/3	2/3	0.0269(1)	0.65(4)
$M3$ (Co^{2+})	1/3	2/3	0.0269(1)	0.35(4)
$M4$ (Al^{3+})	1/3	2/3	0.1880(6)	0.605(7)
$M4$ (Ti^{4+})	1/3	2/3	0.1880(6)	0.395(7)
$M5$ (Al^{3+})	0.1671(2)	0.3342(4)	0.89246(6)	0.950(8)
$M5$ (Ti^{4+})	0.1671(2)	0.3342(4)	0.89246(6)	0.026(4)
$M5$ (Co^{4+})	0.1671(2)	0.3342(4)	0.89246(6)	0.024(4)
O1	0	0	0.1498(1)	1
O2	0.33333	0.66667	0.9413(1)	1
O3	0.1815(2)	0.3632(4)	1/4	1
O4	0.1514(1)	0.3029(2)	0.05343(5)	1
O5	0.5046(1)	0.0092(2)	0.15005(4)	1

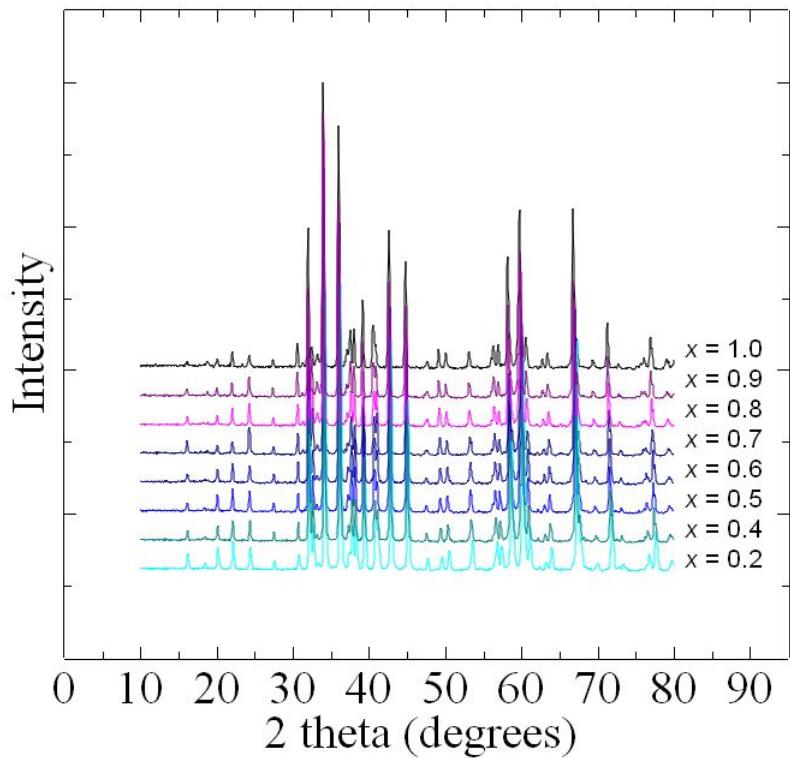


Figure S3. X-ray diffraction patterns of $\text{CaAl}_{12-2x}\text{Co}_x\text{Ti}_x\text{O}_{19}$.

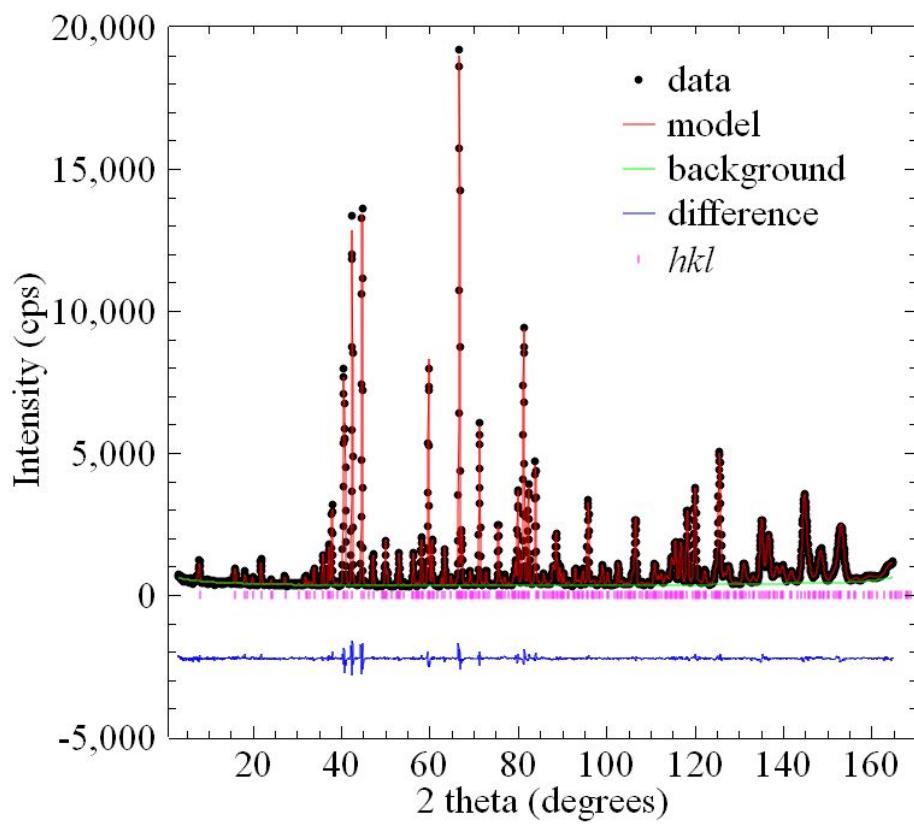


Figure S4. Rietveld refinement model and data of $\text{CaAl}_{10.6}\text{Co}_{0.7}\text{Ti}_{0.7}\text{O}_{19}$.