

Tuning structure and magnetic order through the Cr-substitution in $\text{Co}_3\text{O}_2\text{BO}_3$ Ludwigite

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1. Supplementary material

1.1. *X-ray diffraction Tables*

1.2. *Exchange integrals Table*

References

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Table 1: Crystal structure data of $\text{Co}_{2.22}\text{Cr}_{0.78}\text{O}_2\text{BO}_3$ Ludwigite

Empirical formula	$\text{Co}_{2.22}\text{Cr}_{0.78}\text{O}_2\text{BO}_3$
Formula weight	262.18
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	Pbam
Unit cell dimensions	
$\alpha = 90^\circ$	a=9.3170(5) Å
$\beta = 90^\circ$	b=12.1435(6) Å
$\gamma = 90^\circ$	c=3.0185(2) Å
Volume	341.52(3) Å ³
Z	4
Density (calculated)	5.099 mg/m ³
Absorption coefficient	12.979 mm ⁻¹
F(000)	495
Crystal size	0.121 x 0.020 x 0.019 mm ³
Theta range for data collection	2.756 to 34.140°
Index ranges	-13 ≤ h ≤ 14 -19 ≤ k ≤ 19 -4 ≤ l ≤ 4
Reflections collected	10780
Independent reflections	817 [R(int)=0.0600]
Completeness to theta=25.242°	99.7 %
Absorption correction	Numerical Mu Calculated
Max. and min. transmission	0.91671 and 0.68744
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	817 / 0 / 60
Goodness-of-fit on F ²	1.150
Final R indices [I>2sigma(I)]	R1 = 0.0277, wR2 = 0.0515
R indices (all data)	R1 = 0.0442, wR2 = 0.0618
Extinction coefficient	0.0052(9)
Largest diff. peak and hole	1.841 and -1.380 e.Å ⁻³

Table 2: Atomic coordinates and equivalent isotropic displacement parameters (Å²×10³) for single crystal of $\text{Co}_{2.22}\text{Cr}_{0.78}\text{O}_2\text{BO}_3$ Ludwigite. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Ion (site)	x	y	z	Occu	U(eq)
Co(1)	0.5000	0.5000	1.0000	1.000	7(1)
Co(2)	0.5000	0	0.5000	0.790	7(1)
Cr(2)	0.5000	0	0.5000	0.210	7(1)
Co(3)	0.4981(1)	0.2217(1)	1.0000	1.000	7(1)
Co(4)	0.7403(1)	0.3863(1)	0.5	0.330	6(1)
Cr(4)	0.7403(1)	0.3863(1)	0.5	0.670	6(1)
O(1)	0.3819(3)	0.0775(2)	1.0	1.000	9(1)
O(2)	0.6095(3)	0.3578(2)	1.0000	1.000	8(1)
O(3)	0.6212(3)	0.1397(2)	0.5000	1.000	9(1)
O(4)	0.6546(3)	0.5411(2)	0.5000	1.000	10(1)
O(5)	0.8416(3)	0.2376(2)	0.5000	1.000	9(1)
B(1)	0.7316(4)	0.6374(4)	0.5000	1.000	5(1)

Table 3: Phases identification obtained from Rietveld refinement of $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites. The phase identification were performed using Fullprof and EVA software [1, 2].

Empirical formula	ludwigite	CoO	Co_3O_4	CoCr_2O_4
$\text{Co}_{2.9}\text{Cr}_{0.1}\text{O}_2\text{BO}_3$	97.67%	2.33%	-	-
$\text{Co}_{2.8}\text{Cr}_{0.2}\text{O}_2\text{BO}_3$	94.01%	5.99%	-	-
$\text{Co}_{2.7}\text{Cr}_{0.3}\text{O}_2\text{BO}_3$	100%	-	-	-
$\text{Co}_{2.6}\text{Cr}_{0.4}\text{O}_2\text{BO}_3$	95.95%	1.93%	2.12%	-
$\text{Co}_{2.5}\text{Cr}_{0.5}\text{O}_2\text{BO}_3$	98.85%	0.90%	1.34%	-
$\text{Co}_{2.4}\text{Cr}_{0.6}\text{O}_2\text{BO}_3$	95.01%	0.53%	4.46%	-
$\text{Co}_{2.3}\text{Cr}_{0.7}\text{O}_2\text{BO}_3$	98.72%	-	-	1.28%
$\text{Co}_{2.2}\text{Cr}_{0.8}\text{O}_2\text{BO}_3$	94.33%	-	-	5.67%
$\text{Co}_{2.1}\text{Cr}_{0.9}\text{O}_2\text{BO}_3$	94.01%	-	-	5.99%
$\text{Co}_{2.0}\text{Cr}_{1.0}\text{O}_2\text{BO}_3$	91.56%	-	-	8.44%

Table 4: Crystallographic data obtained through Rietveld refinement of $\text{Co}_{3-x}\text{Cr}_x\text{O}_2\text{BO}_3$ Ludwigites.

Stoichiometric formula	a (Å)	b (Å)	c (Å)	Volume (Å ³)	M. Mass (g/mol)	R_p	R_{wp}	R_{exp}	Chi ²
$\text{Co}_3\text{O}_2\text{BO}_3$ [3]	9.302	11.957	2.972	330.55	267.59	-	-	-	-
$\text{Co}_{2.91}\text{Cr}_{0.09}\text{O}_2\text{BO}_3$	9.2941	11.9702	2.9778	331.58	266.90	1.84	2.64	1.09	5.86
$\text{Co}_{2.80}\text{Cr}_{0.20}\text{O}_2\text{BO}_3$	9.2876	12.0007	2.9893	333.85	266.20	1.99	2.61	1.80	2.09
$\text{Co}_{2.72}\text{Cr}_{0.28}\text{O}_2\text{BO}_3$	9.2858	12.0303	2.9969	335.09	265.58	1.90	2.44	1.84	1.75
$\text{Co}_{2.63}\text{Cr}_{0.37}\text{O}_2\text{BO}_3$	9.2891	12.0653	3.0062	336.92	264.81	1.54	2.05	1.15	3.18
$\text{Co}_{2.50}\text{Cr}_{0.50}\text{O}_2\text{BO}_3$	9.2934	12.0847	3.0097	338.01	264.12	1.70	2.17	1.75	1.54
$\text{Co}_{2.37}\text{Cr}_{0.63}\text{O}_2\text{BO}_3$	9.2986	12.1161	3.0154	339.72	263.85	2.06	2.63	1.94	1.84
$\text{Co}_{2.27}\text{Cr}_{0.73}\text{O}_2\text{BO}_3$	9.3035	12.1247	3.0171	340.33	262.73	1.75	2.20	1.89	1.35
$\text{Co}_{2.20}\text{Cr}_{0.80}\text{O}_2\text{BO}_3$	9.3083	12.138	3.0193	341.13	262.04	1.69	2.11	1.87	1.28
$\text{Co}_{2.09}\text{Cr}_{0.91}\text{O}_2\text{BO}_3$	9.3154	12.1556	3.0227	342.27	261.34	1.64	2.05	1.75	1.37
$\text{Co}_{2.02}\text{Cr}_{0.98}\text{O}_2\text{BO}_3$	9.3205	12.164	3.0237	342.81	260.65	1.77	2.23	1.90	1.38

Table 5: Expressions for calculation the superexchange integrals J_λ and weight of each type of the interacting pair in J_λ .

J_λ	Interacting pair	Expression	weight
J_1	$\text{Co}^{2+}\text{-Co}^{2+}$	$\frac{1}{9} J_{Co^{2+}} [\frac{16}{3}bc + 2c^2]$	1
J_2	$\text{Co}^{2+}\text{-Co}^{2+}$	$\frac{1}{9} [c^2 J_{Co^{2+}} + \frac{4}{3}bc J_{Co^{2+}} - \frac{8}{3}bc \Delta pd_{Co^{2+}}] \sin(\gamma)$	1
J_3	$\text{Co}^{2+}\text{-Co}^{3+}$	$\frac{1}{12} [(\frac{11}{6}bc) J_{Co^{3+}} + (\frac{7}{3}bc + c^2) J_{Co^{2+}} - (\frac{5}{3}bc + 2bc + \frac{c^2}{2})(\Delta pd_{Co^{2+}} + \Delta pd_{Co^{3+}})]$	0.225
	$\text{Co}^{2+}\text{-Co}^{3+}$	$\frac{1}{9} [(\frac{3}{2} J_{Co^{2+}} + (\frac{5}{6}bc + bc) J_{Co^{3+}} - (\frac{5}{3}bc + 2bc + \frac{c^2}{2})(\Delta pd_{Co^{2+}} + \Delta pd_{Co^{3+}})]$	0.67
	$\text{Co}^{2+}\text{-Co}^{2+}$	$\frac{1}{9} [(\frac{15}{6}bc + 3bc + \frac{c^2}{2}) J_{Co^{2+}} - (\frac{5}{6}bc + bc + \frac{c^2}{2}) \Delta pd_{Co^{2+}}]$	0.105
J_4	$\text{Co}^{2+}\text{-Co}^{2+}$	$\frac{1}{9} J_{Co^{2+}} [\frac{16}{3}bc + 2c^2]$	0.624
	$\text{Co}^{2+}\text{-Cr}^{3+}$	$\frac{1}{9} [c^2 J_{Co^{2+}} - (\frac{2}{3}bc + c^2 + 2bc)(\Delta pd_{Co^{2+}} + \Delta pd_{Cr^{3+}}]$	0.331
	$\text{Cr}^{3+}\text{-Cr}^{3+}$	$\frac{1}{9} [\frac{4}{3} J_{Cr^{3+}} + 4bc J_{Cr^{3+}} - 4c^2 \Delta pd_{Cr^{3+}}]$	0.044
J_5	$\text{Co}^{2+}\text{-Co}^{2+}$	$\frac{1}{9} [(\frac{5}{3}bc + 2bc + c^2) J_{Co^{2+}} - (\frac{5}{3}bc + 2bc)(2\Delta pd_{Co^{2+}})]$	0.79
	$\text{Co}^{2+}\text{-Cr}^{3+}$	$\frac{1}{9} [\frac{3}{2}c^2 J_{Co^{2+}} + (\frac{5}{6}bc + bc) J_{Cr^{3+}} - (\frac{5}{3}bc + 2bc + \frac{c^2}{2})(\Delta pd_{Co^{2+}} + \Delta pd_{Cr^{3+}})]$	0.21
J_6	$\text{Co}^{2+}\text{-Co}^{3+}$	$\frac{1}{12} [2c^2 J_{Co^{2+}} + (\frac{8}{3}bc) J_{Co^{3+}} - (\frac{8}{3}bc)(\Delta pd_{Co^{2+}} + U \Delta pd_{Co^{3+}})]$	0.178
	$\text{Co}^{2+}\text{-Co}^{3+}$	$\frac{1}{9} [c^2 J_{Co^{2+}} - (\frac{2}{3}bc + c^2 + 2bc)(\Delta pd_{Co^{2+}} + \Delta pd_{Co^{3+}})]$	0.545
	$\text{Cr}^{3+}\text{-Cr}^{3+}$	$\frac{1}{9} [\frac{4}{3}bc J_{Cr^{3+}} + 4bc J_{Cr^{3+}} - 4c^2 \Delta pd_{Cr^{3+}}]$	0.141
	$\text{Cr}^{3+}\text{-Co}^{2+}$	$\frac{1}{12} [c^2 J_{Co^{2+}} + (\frac{2}{3}bc + 2bc) J_{Cr^{3+}} - (\frac{2}{3}bc + c^2 + 2bc)(\Delta pd_{Co^{2+}} + \Delta pd_{Cr^{3+}})]$	0.047
	$\text{Co}^{2+}\text{-Co}^{2+}$	$\frac{1}{9} [(\frac{2}{3}bc + 2bc + c^2) J_{Co^{2+}} - (\frac{2}{3}bc + 2bc) 2\Delta pd_{Co^{2+}}]$	0.083
J_7	$\text{Co}^{2+}\text{-Co}^{2+}$	$\frac{1}{9} J_{Co^{2+}} [\frac{16}{3}bc + 2c^2]$	1
J_8	$\text{Co}^{2+}\text{-Co}^{3+}$	$\frac{1}{12} [c^2 J_{Co^{2+}} + \frac{1}{3}bc J_{Co^{3+}} - \frac{4}{3}bc(\Delta pd_{Co^{2+}} + \Delta pd_{Co^{3+}})] \sin \gamma$	0.225
	$\text{Co}^{2+}\text{-Cr}^{3+}$	$\frac{1}{9} [c^2 J_{Co^{2+}} + \frac{2}{3}bc J_{Cr^{3+}} - \frac{1}{3}bc(\Delta pd_{Co^{2+}} + \Delta pd_{Cr^{3+}})] \sin \gamma$	0.67
	$\text{Co}^{2+}\text{-Co}^{2+}$	$\frac{1}{9} [(bc + c^2) J_{Co^{2+}} - \frac{2}{3}bc 2\Delta pd_{Co^{2+}}] \sin \gamma$	0.105
J_9	$\text{Co}^{2+}\text{-Co}^{3+}$	$\frac{1}{12} [(\frac{11}{6}bc) J_{Co^{3+}} + (\frac{7}{3}bc + c^2) J_{Co^{2+}} - (\frac{11}{3}bc + \frac{c^2}{2})(\Delta pd_{Co^{2+}} + \Delta pd_{Co^{3+}})]$	0.225
	$\text{Co}^{2+}\text{-Cr}^{3+}$	$\frac{1}{9} [\frac{3}{2}c^2 J_{Co^{2+}} + (\frac{11}{6}bc) J_{Cr^{3+}} - (\frac{11}{3}bc + \frac{c^2}{2})(\Delta pd_{Co^{2+}} + \Delta pd_{Cr^{3+}})]$	0.67
	$\text{Co}^{2+}\text{-Co}^{2+}$	$\frac{1}{9} [(\frac{33}{6}bc + \frac{c^2}{2}) J_{Co^{2+}} - (\frac{11}{6}bc + \frac{c^2}{2}) \Delta pd_{Co^{2+}}]$	0.105
J_{10}	$\text{Co}^{2+}\text{-Co}^{3+}$	$\frac{1}{12} [c^2 J_{Co^{2+}} - (\frac{16}{9}b^2 + c^2)(\Delta pd_{Co^{2+}} + \Delta pd_{Co^{3+}})] \cos \gamma$	0.178
	$\text{Co}^{2+}\text{-Cr}^{3+}$	$\frac{1}{9} [c^2 J_{Co^{2+}} + (\frac{16}{9}b^2) J_{Cr^{3+}} - c^2(\Delta pd_{Co^{2+}} + \Delta pd_{Cr^{3+}})] \cos \gamma$	0.545
	$\text{Cr}^{3+}\text{-Cr}^{3+}$	$\frac{1}{9} [(-4c^2 \Delta pd_{Cr^{3+}})] \cos \alpha$	0.141
	$\text{Cr}^{3+}\text{-Co}^{3+}$	$\frac{1}{12} [\frac{c^2}{2} J_{Co^{3+}} + (\frac{16}{18}b^2) J_{Cr^{3+}} - c^2(\Delta pd_{Co^{3+}} + \Delta pd_{Cr^{3+}})] \cos \gamma$	0.047
	$\text{Co}^{2+}\text{-Co}^{2+}$	$\frac{1}{9} [c^2 J_{Co^{2+}} - (\frac{16}{9}b^2) 2\Delta pd_{Co^{2+}}] \cos \gamma$	0.083
J_{11}	$\text{Cr}^{3+}\text{-Co}^{3+}$	$\frac{1}{12} [c^2 J_{Co^{3+}} + (\frac{8}{3}bc) J_{Cr^{3+}} - (\frac{8}{3}bc + c^2)(\Delta pd_{Co^{3+}} + \Delta pd_{Cr^{3+}})]$	0.302
	$\text{Co}^{3+}\text{-Co}^{3+}$	$\frac{1}{16} [2c^2 J_{Co^{3+}} - (\frac{16}{3}bc) \Delta pd_{Co^{3+}}]$	0.501
	$\text{Cr}^{3+}\text{-Cr}^{3+}$	$\frac{1}{9} [\frac{16}{3}bc J_{Cr^{3+}} - 4c^2 \Delta pd_{Cr^{3+}}]$	0.449
	$\text{Co}^{2+}\text{-Co}^{2+}$	$-\frac{1}{9} [\frac{32}{3}bc \Delta pd_{Co^{2+}}]$	0.011
	$\text{Co}^{2+}\text{-Cr}^{3+}$	$\frac{1}{9} [2c^2 J_{Co^{2+}} + (\frac{8}{3}bc) J_{Cr^{3+}} - (\frac{8}{3}bc)(\Delta pd_{Co^{2+}} + \Delta pd_{Cr^{3+}})]$	0.141
	$\text{Co}^{2+}\text{-Co}^{3+}$	$\frac{1}{12} [c^2 J_{Co^{2+}} - (\frac{16}{3}bc)(\Delta pd_{Co^{2+}} + \Delta pd_{Co^{3+}})]$	0.047