Polymorphism and temperature-induced phase transitions of $Na_2CoP_2O_7$

Supplementary information

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Table S1. Literature data on thermal treatment and resulting crystal structure of $Na_2CoP_2O_7$

Synthesis conditions	Sample form and reported crystal structure	Reference
1. Heating mixture $Na_4P_2O_7$+$Co_2P_2O_7$ or $NaHCO_3$+CoO+$(NH_4)_3PO_4$ to 600 °C 2. Crystallization at 520 °C	Blue powder Tetragonal, a = 7.698(2) Å, c = 10.282(2) Å	[1]
Heating mixture Na_2CO_3+$CoNO_3{\cdot}6H_2O$+$2(NH_4)_2HPO_4$ to 873 K	Blue powder with traces of 'rose' form	[2]
Slow cooling of $Na_2CoP_2O_7$ melt from 973 K	Single crystals of the 'blue' form Orthorhombic $P2_1cn$, a = 7.713 Å, b = 10.271(4) Å, c = 15.378 Å, V = 1218.2(8) Å^3	[2]
Slow cooling of $Na_2CoP_2O_7$ melt from 1073 K	Single crystals of the 'rose' phase Triclinic $P1$, a = 9.735 Å, b = 10.940(3) Å, c = 12.289 Å, α = 148.78°, β = 121.76(1)°, γ = 68.38°, V = 566.8(2) Å^3	[2]
Annealing 'rose' phase at 873 K	'blue' phase	[2]
Heating mixture $NaNO_3$+$Co(CH_3CO_2){\cdot}4H_2O$+$NH_4H_2PO_4$ to 1070 K, cooling to 873 K, quenching to room temperature	Single crystals of the tetragonal form Tetragonal $P4_2/mnm$, a = 7.7058(12) Å, c = 10.301(2) Å, V = 611.6(2) Å^3	[3]
Heating mixture NaH_2PO_4+CoC_2O_4 at 600 °C	Blue powder Orthorhombic $Pna2_1$, a = 15.4061(3) Å, b = 10.28854(9) Å, c = 7.70316(15) Å, V = 1221.00(3) Å^3	[4, 5]

Table S2. Crystal structural parameter for $Na_2CoP_2O_7$ at 300 K refined against NPD data. Space group *Pna*2$_1$ (# 33). Numbers in parentheses are standard deviations of the last significant digit. a = 15.4075(8) Å, b = 10.2901(4) Å, c = 7.7033(4) Å, V = 1221.31(10) Å^3, overall isotropic temperature factor B = 1.05(5) Å^2.

Atom	Wyckoff site	*x*	*y*	*z*	BVS
Co1	4*a*	0.134(3)	0.510(4)	-0.522(6)	1.89
Co2	4*a*	0.1240(16)	0.016(3)	-0.547(6)	1.98
P1	4*a*	0.1914(5)	0.0693(7)	-0.9051(10)	5.13
P2	4*a*	0.0621(5)	0.0495(7)	-0.1870(10)	4.97
P3	4*a*	0.0543(5)	0.4640(7)	-0.1502(10)	5.24
P4	4*a*	0.1937(5)	0.4822(6)	-0.8996(11)	5.09
Na1	4*a*	0.297(3)	0.2553(20)	-0.691(6)	0.82
Na2	4*a*	-0.0724(10)	0.2309(18)	-0.383(4)	0.89
Na3	4*a*	0.2298(16)	0.2876(17)	-0.230(4)	0.94
Na4	4*a*	0.0090(12)	0.241(2)	-0.877(3)	1.03
O1	4*a*	0.1385(6)	0.1027(11)	-0.0712(13)	2.40
O2	4*a*	0.1402(9)	0.1206(13)	-0.7495(16)	1.95
O3	4*a*	0.2857(5)	0.1086(13)	0.101(2)	2.31
O4	4*a*	0.1871(10)	-0.0766(7)	-0.887(2)	1.85
O5	4*a*	0.0696(10)	-0.0965(8)	-0.184(2)	1.75
O6	4*a*	0.0817(10)	0.1200(15)	-0.3601(14)	1.87
O7	4*a*	-0.0164(7)	0.1040(15)	-0.092(2)	2.05
O8	4*a*	0.1075(6)	0.4322(12)	-0.9862(12)	2.46
O9	4*a*	-0.0350(7)	0.3973(15)	-0.135(2)	1.87
O10	4*a*	0.0468(10)	0.6081(8)	-0.157(3)	1.67
O11	4*a*	0.0945(10)	0.4082(18)	-0.3113(17)	1.92
O12	4*a*	0.1878(12)	0.4135(13)	-0.7243(13)	1.91
O13	4*a*	0.2712(7)	0.4238(13)	-0.9919(20)	2.06
O14	4*a*	0.1948(9)	0.6280(7)	-0.905(3)	1.89

Table S3. Crystal structural parameter for $Na_2CoP_2O_7$ at 340 K refined against NPD data. Space group $P4_2/mnm$ (# 136). Numbers in parentheses are standard deviations of the last significant digit. a = 7.71080(18) Å, c = 10.2840(2) Å, V = 611.45(2) Å^3.

Atom	Wyckoff site	x	y	z	Atomic displacement parameters, Å^2	BVS
Co	4*d*	1/2	0	1/4	$U_{11} = U_{22} = 0.024(10)$, $U_{33} = 0.13(3)$, $U_{12} = U_{23} = U_{13} = 0$	1.98
P	8*j*	0.3614(7)	0.016(3)	0.040(4)	$U_{11} = U_{22} = 0.039(3)$, $U_{33} = 0.042(5)$, $U_{12} = -0.039(6)$, $U_{23} = -U_{13} = 0.014(4)$	5.24
Na1	4*g*	0.1442(15)	0.0693(7)	0.065(4)	$U_{iso} = 0.065(4)$	0.84
Na2	4*f*	0.1988(13)	0.0495(7)	0.065(4)	$U_{iso} = 0.065(4)$	0.97
O1	8*j*	0.3630(6)	0.4640(7)	0.047(4)	$U_{11} = U_{22} = 0.056(4)$, $U_{33} = 0.030(5)$, $U_{12} = 0.010(5)$, $U_{23} = -U_{13} = 0.007(3)$	1.83
O2	16*k*	0.1974(6)	0.4822(6)	0.076(5)	$U_{11} = 0.133(7)$, $U_{22} = 0.037(4)$, $U_{33} = 0.057(4)$, $U_{12} = -0.049(3)$, $U_{13} = 0.004(5)$, $U_{23} = -0.007(3)$	2.07
O3	4*e*	1/2	1/2	0.103(8)	$U_{11} = U_{22} = 0.153(8)$, $U_{33} = 0.003(8)$, $U_{12} = 0.099(11)$, $U_{23} = U_{13} = 0$	2.31

References

1. Gabelica-Robert, M. Sur une nouvelle famille de pyrophosphates, pyroarseniates et pyrovanadates du type $A_2BX_2O_7$. *C. R. Acad. Sci. Paris Serie II* **1981,** 293, 497-499.
2. Erragh, F.; Boukhari, A.; Elouadi, B.; Holt, E. M. Crystal structures of 2 allotropic forms of $Na_2CoP_2O_7$. *Journal of Crystallographic and Spectroscopic Research* **1991,** 21 (3), 321-326 DOI: 10.1007/bf01156084.
3. Sanz, F.; Parada, C.; Rojo, J. M.; Ruiz-Valero, C.; Saez-Puche, R. Studies on Tetragonal $Na_2CoP_2O_7$, a Novel Ionic Conductor. *J. Solid State Chem.* **1999,** 145 (2), 604-611 DOI: 10.1006/jssc.1999.8249.
4. Barpanda, P.; Avdeev, M.; Ling, C. D.; Lu, J.; Yamada, A. Magnetic structure and properties of the $Na_2CoP_2O_7$ pyrophosphate cathode for sodium-ion batteries: a supersuperexchange-driven non-collinear antiferromagnet. *Inorg. Chem.* **2013,** 52 (1), 395-401 DOI: 10.1021/ic302191d.
5. Barpanda, P.; Lu, J.; Ye, T.; Kajiyama, M.; Chung, S.-C.; Yabuuchi, N.; Komaba, S.; Yamada, A. A layer-structured $Na_2CoP_2O_7$ pyrophosphate cathode for sodium-ion batteries. *Rsc Advances* **2013,** 3 (12), 3857-3860.