

“Synthesis and Characterization of [(CH₃)₂NH₂][Na_{0.5}Cr_{0.5}(HCOO)₃]: Rare Example of Luminescent Metal-Organic Framework Based on Cr(III) Ions”,

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Table S1. Data collection, cell, and refinement parameters for the single crystal X-ray diffraction studies carried out at 302 and 115 K.

formula	C ₅ H ₁₁ Cr _{0.5} N ₂ Na _{0.5}	C ₅ H ₁₁ Cr _{0.5} N ₂ Na _{0.5} O ₁₂
Fw	218.64	218.64
T, K	302(2) K	115(2) K
wavelength	0.71073 Å	0.71073 Å
crystal system	trigonal	trigonal
space group	R-3	R-3
a, Å	8.3280(12)	8.3121(12)
b, Å	8.3280(12)	8.3121(12)
c, Å	23.012(5)	22.778(5)
α, °	90	90
β, °	90	90
γ, °	120	120
V, Å ³	1382.2(4)	1362.9(4)
Z	6	6
F(000)	681	681
D _c , g/cm ³	1.576	1.598
Θ _{min} , Θ _{max} , °	2.96, 29.43	2.97, 29.58
index ranges	-11 ≤ h ≤ 11	-11 ≤ h ≤ 10
	-11 ≤ k ≤ 10,	-10 ≤ k ≤ 11
	-31 ≤ l ≤ 28	-26 ≤ l ≤ 30
reflections collected	5573	4546
unique reflns., R _{int}	834, 0.0292	830, 0.0841

Completeness to Θ = 29.43	97.1 %	96.6 %
Data / restraints / parameters	834 / 0 / 47	830 / 0 / 47
Goodness of fit on F^2	1.091	1.098
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0372$ $wR_2 = 0.0974$	$R_1 = 0.0686$ $wR_2 = 0.1131$
R indices (all data)	$R_1 = 0.0503$ $wR_2 = 0.1005$	$R_1 = 0.1203$ $wR_2 = 0.1299$
largest diff. peak and hole, e \AA^3	0.455 and -0.538	0.620 and -0.547

Table S2. IR and Raman frequencies (in cm^{-1}) of DMNaCr and suggested assignments.^a

Raman 294 K	Raman 80 K	IR 295 K	IR 5 K	assignment
		3126s	3134m	$\nu(\text{NH}_2)$
		3065sh	3071m	$\nu(\text{NH}_2)$
3048sh	3046m		3038w	$\nu_{\text{as}}(\text{CH}_3)$
3038m	3035m	3034w	3028w	$\nu_{\text{as}}(\text{CH}_3)$
		3007sh	3012m,b	$\nu(\text{NH}_2)$
2971s	2971s	2975w	2974w	$\nu_{\text{s}}(\text{CH}_3)$
2035vw	2939w	2936vw	2945m	$\nu_{\text{s}}(\text{CH}_3)$
2905vw	2906vw			$\nu_4(\text{HCOO}^-) + \nu_5(\text{HCOO}^-)$
2873m	2880sh, 2870m	2873s	2882sh, 2866s	$\nu_1(\text{HCOO}^-)$
2858m	2855w	2860s	2856s	
2822w	2816w			$\nu(\text{NH}_2)$
		2791s	2828m, 2812w	$\nu(\text{NH}_2)$
			2777s	
2737w	2741w	2741vw	2742w	$2\nu_5(\text{HCOO}^-)$
		2567w, 2499w	2583vw, 2537w	$\rho(\text{NH}_2) + \delta(\text{NH}_2)$
			2524w, 2512w	
		2457w	2471w, 2460w	combinations of $\rho(\text{CH}_3)$, $\delta(\text{CH}_3)$ and $\nu_{\text{as}}(\text{CNC})$
			2454w	
1676m	1674m	1673sh	1676w	$\nu(\text{CO})$
1621w	1622w	1651sh, 1634vs	1652sh, 1635vs	$\nu_4(\text{HCOO}^-)$ and $\delta(\text{NH}_2)$
1585w	1597w	1596s	1609w, 1594s	$\nu_4(\text{HCOO}^-)$
			1573m, 1559w	
			1488w	$\omega(\text{NH}_2)$
1473sh	1483w, 1470w	1471w	1474w	$\delta_{\text{as}}(\text{CH}_3)$
1458w	1456m	1459w	1458w	$\delta_{\text{as}}(\text{CH}_3)$
		1441w	1441w	$\delta_{\text{as}}(\text{CH}_3)$
1435vw	1432w		1433w, 1429w	$\tau(\text{NH}_2)$
1416vw	1416vw	1420vw	1415vw	$\delta_{\text{s}}(\text{CH}_3)$

1376s	1381m, 1373s	1379m	1384w, 1376m	$\nu_5(\text{HCOO}^-)$
1337m	1336m		1339w	$\nu_5(\text{HCOO}^-)$
1318m	1308m	1320s	1315s	$\nu_2(\text{HCOO}^-)$
1292m	1290m, 1279m	1291s	1292s, 1287m 1272sh	$\nu_2(\text{HCOO}^-)$
1233vw	1233w	1257sh	1259sh	$\rho(\text{CH}_3)$
1121vw				$\rho(\text{CH}_3)$
1092w	1095w	1095vw	1098vw	$\rho(\text{CH}_3)$
1057w	1062w	1061vw	1067vw, 1061vw	$\nu_6(\text{HCOO}^-)$
		1046vw	1048vw	$\rho(\text{CH}_3)$
1023w	1024w	1024m	1026m	$\nu_{\text{as}}(\text{CNC})$
		886w,b	907w,b	$\rho(\text{NH}_2)$
890m	892m	893w	895w	$\nu_5(\text{CNC})$
		813s	818s, 813s	$\nu_3(\text{HCOO}^-)$
800m	802m		800w	$\nu_3(\text{HCOO}^-)$
		420m	427m, 420m	$T'(\text{Na}^+)$ and $T'(\text{Cr}^{3+})$
403w	399m	403w	400w	$\delta(\text{CNC})$
342m	347m			$T'(\text{Na}^+)$ and $T'(\text{Cr}^{3+})$
	290vw		296m	$\tau(\text{CH}_3)$
		276m	282m	$T'(\text{Na}^+)$ and $T'(\text{HCOO}^-)$
225w	231w, 215w	247w	253w, 240w	$T'(\text{Na}^+)$ and $T'(\text{HCOO}^-)$
		190s	221w, 204s	$T'(\text{HCOO}^-)$
			198s	
178m	184m		175w	$L(\text{HCOO}^-)$
	152w			$L(\text{DMA})$
110s	108s			$L(\text{HCOO}^-)$
		100w	96w	$T'(\text{DMA})$
60m	65m			$L(\text{HCOO}^-)$

^aKey: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad

Table S3. Energies of emission bands of DMNaCr at 10 K with their tentative assignments to R1, R2, Cr-Cr pair and vibronic bands.

Energy	Rel. intensity	Label
14587.7	3.5	L(HCOO ⁻)
14544.0	76.7	R2
14526.0	51.0	L(HCOO ⁻)
14511.5	52.9	L(HCOO ⁻)
14477.0	52.7	L(HCOO ⁻)
14495.3	100.0	R1
14434.0	19.7	L(HCOO ⁻)
14363.5	29.0	L(HCOO ⁻)
14331.1	39.8	T'(HCOO ⁻)
14256.2	33.9	T'(Na ⁺) and T'(HCOO ⁻)
14200.0	8.8	T'(Na ⁺) and T'(Cr ³⁺)
14166.8	8.6	T'(Na ⁺) and T'(Cr ³⁺)
14118.4	23.0	pair
13947.2	6.8	L(HCOO ⁻)
13796.3	5.0	T'(Na ⁺) and T'(HCOO ⁻)
13772.0	4.4	v ₃ (HCOO ⁻)
13724.3	10.9	pair
13662.0	4.3	v ₃ (HCOO ⁻)
13555.0	3.8	L(HCOO ⁻)
13535.0	3.9	v _{as} (CNC)
13478.1	5.0	v _{as} (CNC)
13409.0	3.2	v ₆ (HCOO ⁻)
13312.0	3.8	ρ(CH ₃)
13252.0	7.5	v ₂ (HCOO ⁻)
13233.8	8.8	pair
13217.0	7.5	v ₂ (HCOO ⁻)
13167.4	5.0	v ₂ (HCOO ⁻)
13155.0	4.5	v ₅ (HCOO ⁻)
13070.0	3.0	δ _s (CH ₃)
12990.0	2.7	v ₄ (HCOO ⁻)
12939.8	3.0	v ₄ (HCOO ⁻)

12910.4	3.2	$\nu_4(\text{HCOO}^-)$
12804.0	2.5	$\nu(\text{CO})$

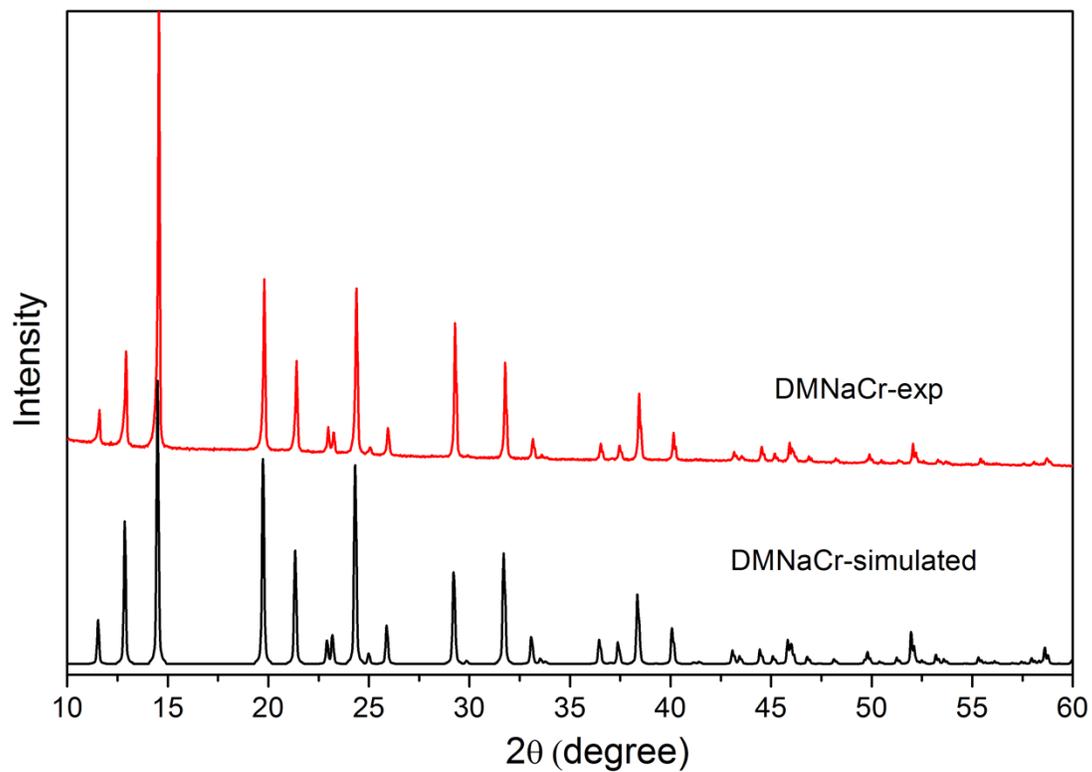


Figure S1. Powder XRD patterns for the as-prepared bulk sample of DMNaCr, with the calculated one based on the single crystal structures at 302 K.

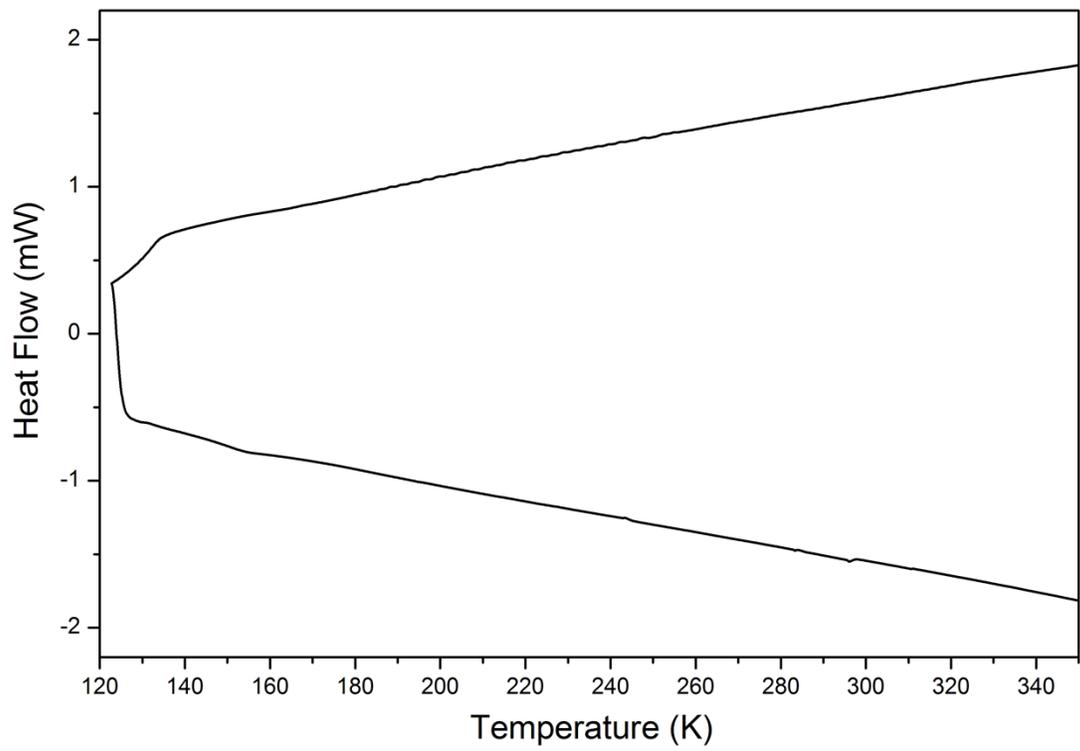


Figure S2. DSC traces for DMNaCr.

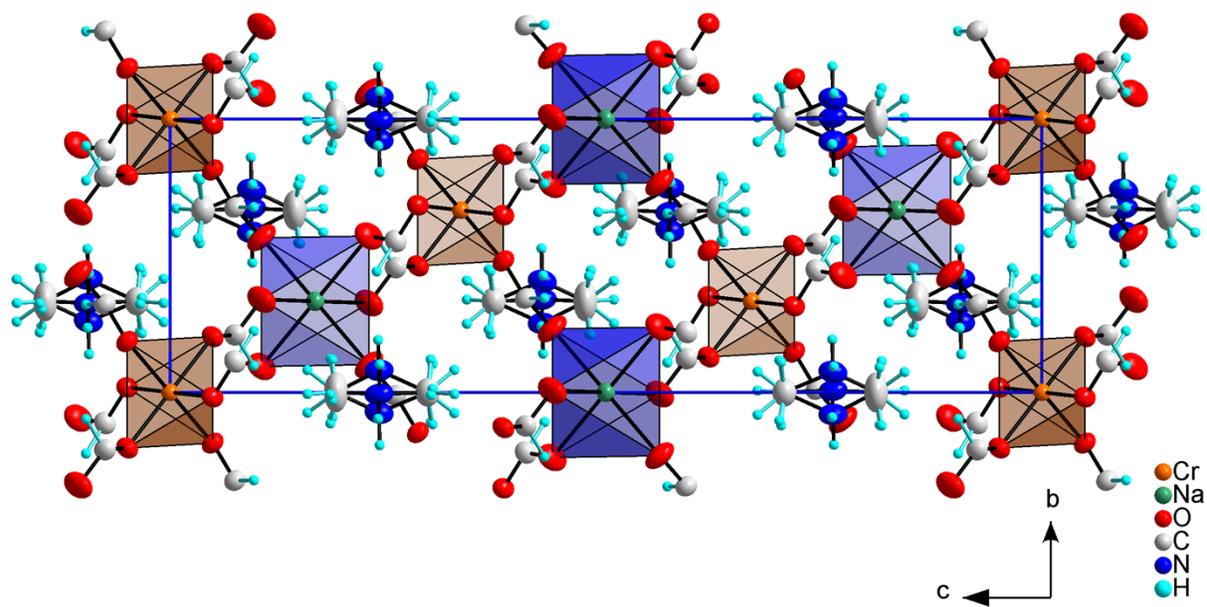


Figure S3. Structure of DMNaCr at 302 K viewed along the *a* axis. Thermal ellipsoids for N atoms of DMA⁺ are shown in blue.

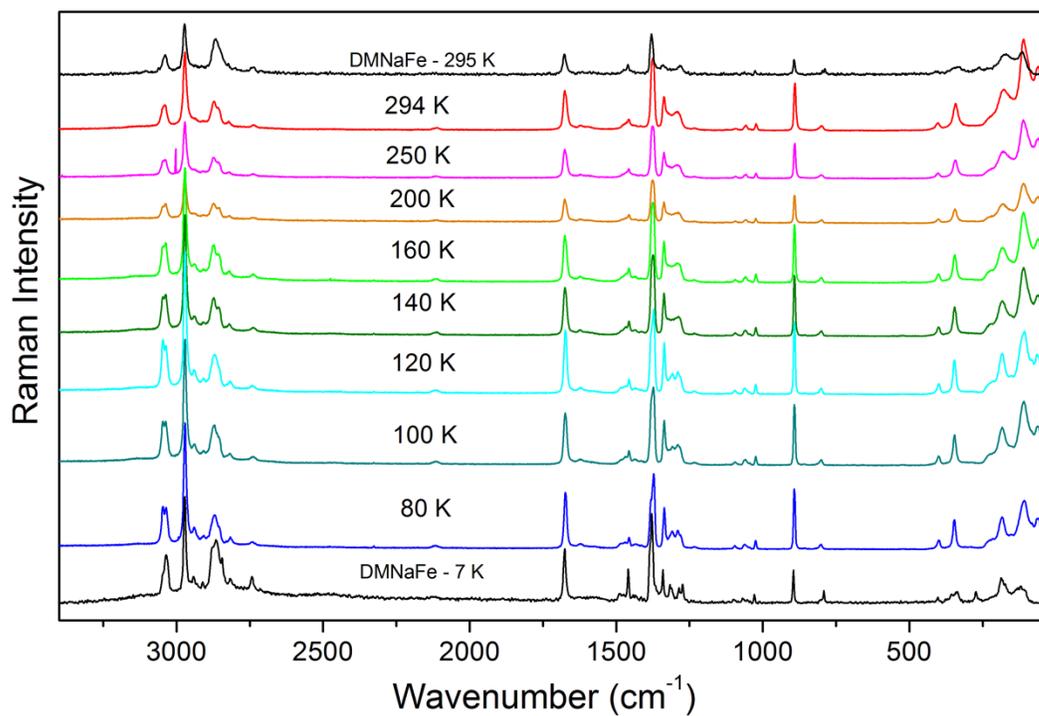


Figure S4. Raman spectra of DMNaCr recorded at various temperatures corresponding to the whole spectral range 50-3400 cm⁻¹. Raman spectra of DMNaFe at 295 and 7 K are also shown for the comparison sake.

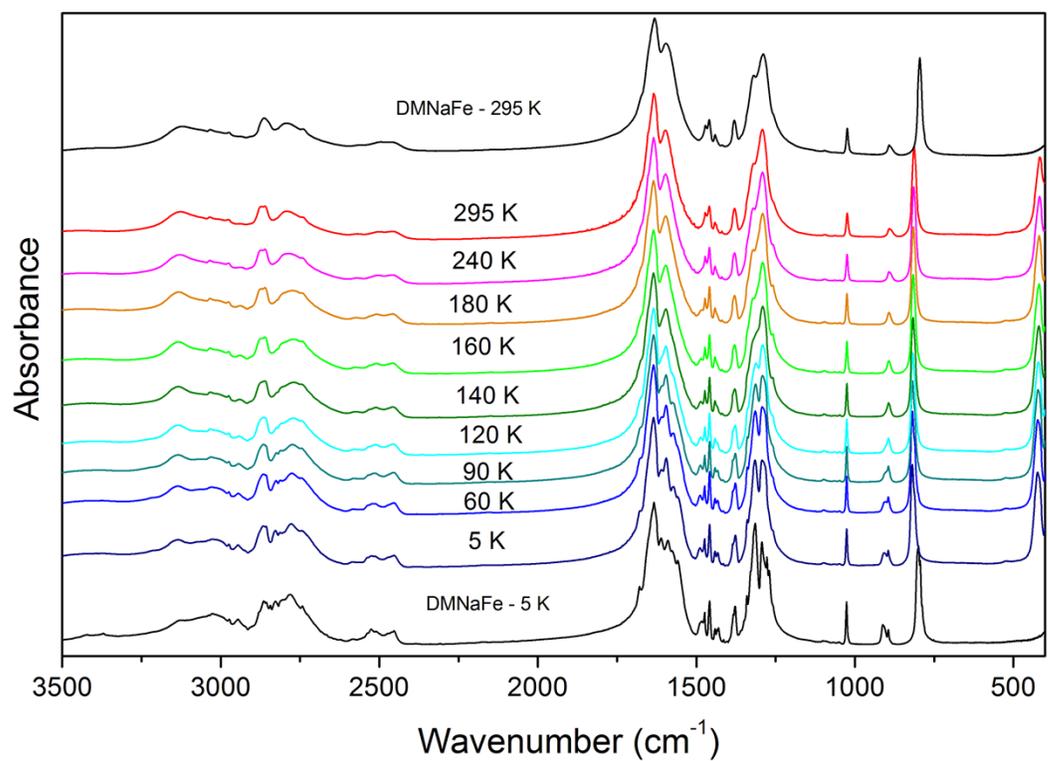


Figure S5. Mid-IR spectra of DMNaCr recorded at various temperatures corresponding to the spectral range 400-3500 cm⁻¹. Mid-IR spectra of DMNaFe at 295 and 5 K are also shown for the comparison sake.

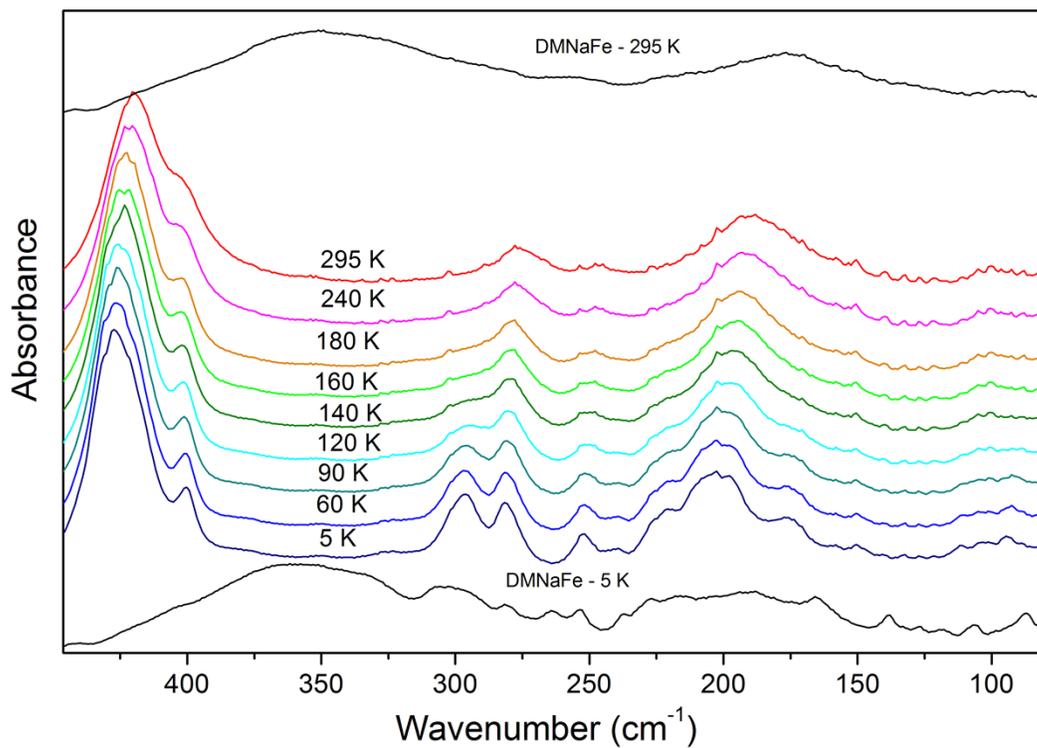


Figure S6. Mid-IR spectra of DMNaCr recorded at various temperatures corresponding to the spectral range 80-480 cm⁻¹. Mid-IR spectra of DMNaFe at 295 and 5 K are also shown for the comparison sake.