"Phase Transitions and Chromium(III) Luminescence in Perovskite-type $[C_2H_5NH_3][Na_{0.5}Cr_xAl_{0.5-x}(HCOO)_3]$ (x=0, 0.025, 0.5), Correlated with Structural, Dielectric and Phonon Properties "

by Maciej Ptak *et al.*

Table S1. Selected bonds (Å) for EtANaCr at 297 and 400 K and for EtANaAl at 270 and 375 K.

EtANaCr at 297 K		EtANaCr at 400 K		EtNaAl at 270 K		EtNaAl at 375 K	
Cr1—O11	1.9724 (12)	Cr1—O1	1.9766 (18)	Al1—O1	1.892 (4)	Al—O1^{xi}	1.890 (2)
Cr1—O7	1.9744 (10)	Cr1—O1^{xi}	1.9767 (18)	Al1—O7	1.894 (4)	Al—O1	1.890 (2)
Cr1—O5	1.9830 (10)	Cr1—O3	1.9805 (19)	Al1—O11	1.895 (5)	Al—O3^{xi}	1.899 (2)
Cr1—O9	1.9831 (10)	Cr1—O3^{xi}	1.9805 (19)	Al1—O9	1.904 (4)	Al—O3	1.899 (2)
Cr1—O1	1.9811 (12)	Cr1—O2	1.9818 (18)	Al1—O5	1.910 (4)	Al—O2	1.903 (2)
Cr1—O3	1.9823 (10)	Cr1—O2^{xi}	1.9818 (18)	Al1—O3	1.911 (4)	Al—O2^{xi}	1.904 (2)
Na—O12^{i}	2.3874 (16)	Na1—O6^{xii}	2.419 (2)	Na—O12^{x}	2.394 (5)	Na—O6^{xii}	2.434 (3)
Na—O8^{ii}	2.4139 (15)	Na1—O6^{xiii}	2.419 (2)	Na—O8^{ix}	2.422 (5)	Na—O6^{xiii}	2.434 (3)
Na—O2^{iii}	2.4345 (16)	Na1—O4	2.439 (2)	Na—O4^{vii}	2.442 (6)	Na—O4	2.452 (2)
Na—O4^{iv}	2.4378 (16)	Na1—O4^{xiv}	2.439 (2)	Na—O2^{vi}	2.445 (5)	Na—O4^{xiv}	2.452 (2)
Na—O6^{v}	2.5195 (13)	Na1—O5^{xv}	2.551 (2)	Na—O6^{viii}	2.526 (4)	Na—O5^{xv}	2.553 (2)
Na—O10	2.5251 (12)	Na1—O5^{xvi}	2.551 (2)	Na—O10	2.527 (4)	Na—O5^{xvi}	2.553 (2)
O1—C5	1.266 (2)	O1—C1	1.268 (3)	O1—C5	1.269 (8)	O1—C1	1.267 (4)
O2—C5	1.224 (2)	O2—C3	1.256 (4)	O2—C5	1.219 (8)	O2—C3	1.264 (4)
O2—Na^{vi}	2.4345 (16)	O3—C2	1.278 (3)	O2—Na^{iii}	2.446 (5)	O3—C2	1.271 (4)
O3—C3	1.259 (2)	O4—C1	1.221 (3)	O3—C3	1.257 (7)	O4—C1	1.219 (4)
O4—C6	1.229 (2)	O5—C3	1.228 (3)	O4—C6	1.233 (8)	O5—C3	1.230 (4)
O4—Na^{vii}	2.4378 (16)	O5—Na1^{xiii}	2.551 (2)	O4—Na^{iv}	2.442 (6)	O5—Na^{xiii}	2.553 (2)
O5—C2	1.2839 (19)	O6—C2	1.209 (4)	O5—C2	1.280 (7)	O6—C2	1.215 (4)
O6—C3	1.235 (2)	O6—Na1^{xv}	2.419 (2)	O6—C3	1.230 (7)	O6—Na^{xv}	2.434 (3)
O6—Na^{viii}	2.5195 (13)	C4—N2	1.4601 (11)	O6—Na^{v}	2.526 (4)	C4—N2	1.4600 (11)
O7—C4	1.274 (2)	C4—C5	1.4995 (11)	O7—C4	1.276 (7)	C4—C5	1.4995 (11)
O8—C4	1.218 (2)	C6—N1	1.4602 (11)	O8—C4	1.217 (7)	C6—N1	1.4601 (11)

O8—Na^{ix}	2.4139 (15)	C6—C7	1.4993 (10)	O8—Na^{ii}	2.422 (5)	C6—C7	1.4995 (10)
O9—C1	1.2606 (19)			O9—C1	1.264 (7)		
O10—C1	1.2413 (19)			O10—C1	1.242 (7)		
O11—C6	1.264 (2)			O11—C6	1.264 (8)		
O12—C2	1.217 (2)			O12—C2	1.224 (7)		
O12—Na^{x}	2.3874 (16)			O12—Na^{i}	2.394 (5)		
N2—C7	1.471 (3)			N2—C7	1.474 (8)		
C7—C8	1.476 (4)			C7—C8	1.483 (11)		
N1—C9	1.478 (3)			N1—C9	1.469 (9)		
C10—C9	1.453 (4)			C10—C9	1.475 (11)		

Symmetry code(s): (i) *x*, *y*+1, *z*; (ii) *x*+1, *y*, *z*; (iii) *x*+1/2, -*y*+1, *z*-1/2; (iv) *x*+1/2, -*y*+1, *z*+1/2; (v) *x*+1, *y*+1, *z*; (vi) *x*-1/2, -*y*+1, *z*+1/2; (vii) *x*-1/2, -*y*+1, *z*-1/2; (viii) *x*-1, *y*-1, *z*; (ix) *x*-1, *y*, *z*; (x) *x*, *y*-1, *z*; (xi) -*x*, -*y*, -*z*+1; (xii) *x*-1/2, -*y*+1/2, *z*-1/2; (xiii) -*x*+1/2, *y*-1/2, -*z*+1/2; (xiv) -*x*, -*y*, -*z*; (xv) -*x*+1/2, *y*+1/2, -*z*+1/2; (xvi) *x*-1/2, -*y*-1/2, *z*-1/2. Standard deviations are given in brackets.

Table S2. Selected angles (°) for EtANaCr at 297 and 400 K and for EtANaAl at 270 and 375 K.

EtANaCr at 297 K			
O11—Cr1—O7	89.21 (5)	O12^{i}—Na—O10	95.08 (6)
O11—Cr1—O5	90.01 (4)	O8^{ii}—Na—O10	89.32 (5)
O7—Cr1—O5	179.10 (5)	O2^{iii}—Na—O10	88.76 (5)
O11—Cr1—O9	89.16 (5)	O4^{iv}—Na—O10	83.93 (5)
O7—Cr1—O9	90.46 (4)	O6^{v}—Na—O10	179.07 (6)
O5—Cr1—O9	89.08 (4)	C5—O1—Cr1	125.91 (11)
O11—Cr1—O1	178.72 (5)	C5—O2—Na^{vi}	118.77 (12)
O7—Cr1—O1	92.07 (4)	C3—O3—Cr1	127.97 (10)
O5—Cr1—O1	88.71 (5)	C6—O4—Na^{vii}	117.80 (12)
O9—Cr1—O1	90.78 (5)	C2—O5—Cr1	125.36 (10)
O11—Cr1—O3	90.80 (5)	C3—O6—Na^{viii}	119.58 (10)
O7—Cr1—O3	89.09 (5)	C4—O7—Cr1	128.73 (11)
O5—Cr1—O3	91.37 (4)	C4—O8—Na^{ix}	122.87 (12)
O9—Cr1—O3	179.55 (5)	C1—O9—Cr1	127.91 (10)
O1—Cr1—O3	89.27 (5)	C1—O10—Na	119.70 (10)
O12^{i}—Na—O8^{ii}	175.00 (6)	C6—O11—Cr1	128.48 (12)

O12^{i}—Na—O2^{iii}	92.49 (6)	C2—O12—Na^{x}	129.48 (12)
O8^{ii}—Na—O2^{iii}	90.00 (5)	O10—C1—O9	125.08 (14)
O12^{i}—Na—O4^{iv}	91.41 (6)	O12—C2—O5	124.00 (16)
O8^{ii}—Na—O4^{iv}	86.67 (6)	O6—C3—O3	125.82 (15)
O2^{iii}—Na—O4^{iv}	172.00 (6)	O8—C4—O7	124.84 (16)
O12^{i}—Na—O6^{v}	84.16 (5)	O2—C5—O1	124.72 (17)
O8^{ii}—Na—O6^{v}	91.47 (5)	O4—C6—O11	125.22 (17)
O2^{iii}—Na—O6^{v}	90.74 (5)	N2—C7—C8	111.0 (2)
O4^{iv}—Na—O6^{v}	96.62 (5)	C10—C9—N1	112.1 (2)
EtANaCr at 400 K			
O1—Cr1—O1^{xi}	180.0	O6^{xii}—Na1—O5^{xv}	86.61 (8)
O1—Cr1—O3	91.02 (8)	O6^{xiii}—Na1—O5^{xv}	93.39 (8)
O1^{xi}—Cr1—O3	88.98 (8)	O4—Na1—O5^{xv}	92.80 (7)
O1—Cr1—O3^{xi}	88.98 (8)	O4^{xiv}—Na1—O5^{xv}	87.20 (7)
O1^{xi}—Cr1—O3^{xi}	91.02 (8)	O6^{xii}—Na1—O5^{xvi}	93.39 (8)
O3—Cr1—O3^{xi}	180.0	O6^{xiii}—Na1—O5^{xvi}	86.61 (8)
O1—Cr1—O2	89.52 (8)	O4—Na1—O5^{xvi}	87.20 (7)
O1^{xi}—Cr1—O2	90.48 (8)	O4^{xiv}—Na1—O5^{xvi}	92.80 (7)
O3—Cr1—O2	89.15 (8)	O5^{xv}—Na1—O5^{xvi}	180.00 (10)
O3^{xi}—Cr1—O2	90.85 (8)	C1—O1—Cr1	128.07 (17)
O1—Cr1—O2^{xi}	90.48 (8)	C3—O2—Cr1	128.95 (19)
O1^{xi}—Cr1—O2^{xi}	89.52 (8)	C2—O3—Cr1	127.4 (2)
O3—Cr1—O2^{xi}	90.85 (8)	C1—O4—Na1	119.06 (18)
O3^{xi}—Cr1—O2^{xi}	89.15 (8)	C3—O5—Na1^{xiii}	120.1 (2)
O2—Cr1—O2^{xi}	180.00 (6)	C2—O6—Na1^{xv}	126.9 (2)
O6^{xii}—Na1—O6^{xiii}	180.00 (13)	O4—C1—O1	125.3 (3)
O6^{xii}—Na1—O4	90.92 (8)	O6—C2—O3	124.7 (3)
O6^{xiii}—Na1—O4	89.08 (8)	O5—C3—O2	126.5 (3)
O6^{xii}—Na1—O4^{xiv}	89.08 (8)	N2—C4—C5	109.9 (4)
O6^{xiii}—Na1—O4^{xiv}	90.92 (8)	N1—C6—C7	110.1 (3)
O4—Na1—O4^{xiv}	180.0		
EtANaAl at 270 K			
O1—Al1—O7	92.00 (18)	O12^{x}—Na—O10	95.69 (18)

O1—Al1—O11	178.4 (2)	O8^{ix}—Na—O10	89.37 (15)
O7—Al1—O11	89.59 (18)	O4^{vii}—Na—O10	83.68 (16)
O1—Al1—O9	90.75 (19)	O2^{vi}—Na—O10	87.95 (16)
O7—Al1—O9	90.59 (18)	O6^{viii}—Na—O10	178.7 (2)
O11—Al1—O9	89.36 (19)	C5—O1—Al1	128.9 (4)
O1—Al1—O5	88.66 (18)	C5—O2—Na^{iii}	117.2 (4)
O7—Al1—O5	179.3 (2)	C3—O3—Al1	130.7 (4)
O11—Al1—O5	89.75 (18)	C6—O4—Na^{iv}	117.0 (4)
O9—Al1—O5	89.39 (19)	C2—O5—Al1	127.0 (4)
O1—Al1—O3	89.56 (19)	C3—O6—Na^{v}	119.2 (4)
O7—Al1—O3	89.02 (19)	C4—O7—Al1	131.8 (4)
O11—Al1—O3	90.34 (19)	C4—O8—Na^{ii}	121.1 (4)
O9—Al1—O3	179.5 (2)	C1—O9—Al1	130.4 (4)
O5—Al1—O3	90.99 (18)	C1—O10—Na	119.5 (4)
O12^{x}—Na—O8^{ix}	174.44 (19)	C6—O11—Al1	130.5 (4)
O12^{x}—Na—O4^{vii}	91.73 (18)	C2—O12—Na^{i}	130.2 (4)
O8^{ix}—Na—O4^{vii}	86.54 (18)	O10—C1—O9	125.7 (6)
O12^{x}—Na—O2^{vi}	92.32 (19)	O12—C2—O5	124.2 (5)
O8^{ix}—Na—O2^{vi}	90.15 (17)	O6—C3—O3	126.9 (6)
O4^{vii}—Na—O2^{vi}	171.03 (19)	O8—C4—O7	124.6 (6)
O12^{x}—Na—O6^{viii}	83.22 (15)	O2—C5—O1	125.4 (6)
O8^{ix}—Na—O6^{viii}	91.75 (17)	O4—C6—O11	124.8 (6)
O4^{vii}—Na—O6^{viii}	97.11 (17)	N2—C7—C8	111.3 (6)
O2^{vi}—Na—O6^{viii}	91.32 (17)	N1—C9—C10	111.5 (7)
EtANaAl at 375 K			
O1^{xi}—Al—O1	180.0	O6^{xii}—Na—O5^{xv}	86.21 (9)
O1^{xi}—Al—O3^{xi}	90.79 (9)	O6^{xiii}—Na—O5^{xv}	93.79 (9)
O1—Al—O3^{xi}	89.21 (9)	O4—Na—O5^{xv}	92.63 (8)
O1^{xi}—Al—O3	89.21 (9)	O4^{xiv}—Na—O5^{xv}	87.37 (8)
O1—Al—O3	90.79 (9)	O6^{xii}—Na—O5^{xvi}	93.79 (9)
O3^{xi}—Al—O3	180.0	O6^{xiii}—Na—O5^{xvi}	86.21 (9)
O1^{xi}—Al—O2	90.31 (9)	O4—Na—O5^{xvi}	87.37 (8)
O1—Al—O2	89.69 (9)	O4^{xiv}—Na—O5^{xvi}	92.63 (8)

O3^{xi}—Al—O2	90.76 (9)	O5^{xv}—Na—O5^{xvi}	180.00 (12)
O3—Al—O2	89.24 (9)	C1—O1—Al	130.3 (2)
O1^{xi}—Al—O2^{xi}	89.69 (9)	C3—O2—Al	131.6 (2)
O1—Al—O2^{xi}	90.31 (9)	C2—O3—Al	130.3 (2)
O3^{xi}—Al—O2^{xi}	89.24 (9)	C1—O4—Na	117.9 (2)
O3—Al—O2^{xi}	90.76 (9)	C3—O5—Na^{xiii}	119.2 (2)
O2—Al—O2^{xi}	180.0	C2—O6—Na^{xv}	125.9 (3)
O6^{xii}—Na—O6^{xiii}	180.00 (14)	O4—C1—O1	124.9 (3)
O6^{xii}—Na—O4	90.92 (9)	O6—C2—O3	124.6 (3)
O6^{xiii}—Na—O4	89.08 (9)	O5—C3—O2	126.7 (3)
O6^{xii}—Na—O4^{xiv}	89.08 (9)	N2—C4—C5	110.1 (3)
O6^{xiii}—Na—O4^{xiv}	90.92 (9)	N1—C6—C7	110.0 (3)
O4—Na—O4^{xiv}	180.0		

Symmetry code(s): (i) *x*, *y*+1, *z*; (ii) *x*+1, *y*, *z*; (iii) *x*+1/2, -*y*+1, *z*-1/2; (iv) *x*+1/2, -*y*+1, *z*+1/2; (v) *x*+1, *y*+1, *z*; (vi) *x*-1/2, -*y*+1, *z*+1/2; (vii) *x*-1/2, -*y*+1, *z*-1/2; (viii) *x*-1, *y*-1, *z*; (ix) *x*-1, *y*, *z*; (x) *x*, *y*-1, *z*; (xi) -*x*, -*y*, -*z*+1; (xii) *x*-1/2, -*y*+1/2, *z*-1/2; (xiii) -*x*+1/2, *y*-1/2, -*z*+1/2; (xiv) -*x*, -*y*, -*z*; (xv) -*x*+1/2, *y*+1/2, -*z*+1/2; (xvi) *x*-1/2, -*y*-1/2, *z*-1/2. Standard deviations are given in brackets.

Table S3. Selected hydrogen-bond parameters.

D*—H···*A	***D*—H (Å)**	**H···*A* (Å)**	***D*···*A* (Å)**	***D*—H···*A* (°)**
EtANaCr at 297 K				
N2—H2C···O6^{i}	0.89	1.99	2.8675 (19)	169.9
N2—H2B···O5^{ii}	0.89	2.10	2.9863 (19)	176.2
N2—H2B···O12^{ii}	0.89	2.53	3.150 (2)	126.8
N2—H2A···O4^{iii}	0.89	2.01	2.8708 (19)	161.7
N1—H1C···O7	0.89	2.15	2.9799 (18)	155.6
N1—H1C···O8	0.89	2.44	3.202 (2)	144.6
N1—H1B···O10^{iv}	0.89	1.98	2.8604 (19)	167.6
N1—H1A···O2^{v}	0.89	2.13	2.959 (2)	155.4
N1—H1A···O1^{v}	0.89	2.59	3.2805 (19)	135.5
EtANaCr at 400 K				
N1A—H2A···O4	0.89	2.14	2.95 (3)	151.6

N1A—H2B···O3^{vi}	0.89	2.37	3.128 (17)	143.5
N1A—H2B···O6^{vi}	0.89	2.48	3.27 (2)	148.4
N1A—H2C···O5^{vii}	0.89	1.94	2.79 (2)	160.2
N1—H1A···O4	0.89	2.09	2.93 (3)	156.2
N1—H1B···O3^{vi}	0.89	2.02	2.914 (13)	177.9
N1—H1B···O6^{vi}	0.89	2.53	3.090 (19)	121.8
N1—H1C···O5^{vii}	0.89	2.07	2.949 (17)	167.5
EtANaAl at 270 K				
C2—H2···O11	0.93	2.48	2.899 (7)	107.7
C4—H4···O1	0.93	2.56	2.993 (7)	108.9
N2—H2A···O4^{v}	0.89	2.00	2.858 (7)	160.7
N2—H2B···O6^{iv}	0.89	1.97	2.848 (7)	171.1
N2—H2C···O5^{viii}	0.89	2.12	3.009 (7)	174.2
N2—H2C···O12^{viii}	0.89	2.50	3.118 (7)	127.2
C7—H7B···O12^{viii}	0.97	2.53	3.052 (8)	113.4
N1—H1A···O2^{iii}	0.89	2.09	2.941 (7)	159.5
N1—H1B···O7	0.89	2.20	3.023 (6)	152.7
N1—H1B···O8	0.89	2.34	3.132 (7)	148.8
N1—H1C···O10^{i}	0.89	1.99	2.850 (7)	163.2
C9—H9B···O9^{i}	0.97	2.51	3.199 (8)	128.3
EtANaAl at 375 K				
C2—H2···O1	0.93	2.53	2.949 (4)	107.7
C4—H4B···O2^{vi}	0.97	2.32	3.102 (9)	137.3
N2—H2A···O4	0.89	2.21	3.01 (3)	149.5
N2—H2B···O3^{vii}	0.89	2.43	3.154 (15)	139.0
N2—H2B···O6^{vii}	0.89	2.36	3.18 (2)	153.1
N2—H2C···O5^{vi}	0.89	1.88	2.732 (18)	160.3
C6—H6A···O6^{vii}	0.97	2.40	2.879 (7)	109.9
C7—H7C···O4^{ix}	0.96	2.58	3.361 (8)	138.4
N1—H1A···O4	0.89	2.02	2.86 (2)	158.7
N1—H1B···O3^{vii}	0.89	2.08	2.972 (11)	175.1
N1—H1B···O6^{vii}	0.89	2.50	3.066 (15)	121.7
N1—H1C···O5^{vi}	0.89	2.09	2.967 (16)	169.2

Symmetry code(s): (i) *x*+1/2, -*y*+1, *z*+1/2; (ii) *x*, *y*+1, *z*; (iii) *x*-1/2, -*y*+1, *z*+1/2; (iv) *x*-1/2, -*y*+1, *z*-1/2; (v) *x*+1/2, -*y*+1, *z*-1/2; (vi) -*x*+1, -*y*, -*z*+1; (vii) *x*+1/2, -*y*+1/2, *z*-1/2; (viii) *x*, *y*-1, *z*; (ix) -*x*+1/2, *y*-1/2, -*z*+1/2. Standard deviations are given in brackets.

Table S4. Room temperature IR and Raman (at 300 and 400 K) wavenumbers (cm^{-1}) measured for EtANaCr and EtANaAlCr compounds.[a]

EtANaCr			**EtANaAlCr**			Assignment
IR (RT)	Raman		IR (RT)	Raman		
	at 300 K	at 400 K		at 300 K	at 400 K	
3155 b,vw	3158 b,vw		3153 b,m			$\nu(NH_3)$
3099 b,vw	3068 b,vw	3051 b,vw	3114 b,m	3082 b,vw	3071 b,vw	$\nu(NH_3)$
	3034 m	3031 m		3035 w	3033 w	$\nu_{as}(CH_3)$ and $\nu_{as}(CH_2)$
	3024 sh,w					$\nu_{as}(CH_3)$ and $\nu_{as}(CH_2)$
3015 vw			3016 vw			$\nu_{as}(CH_3)$ and $\nu_{as}(CH_2)$
2996 w	2994 m	2994 s	2999 w	2996 w	2996 sh,w	$\nu_{as}(CH_3)$ and $\nu_{as}(CH_2)$
2977 w	2976 w	2976 sh,w	2981 w	2978 s	2980 s	$\nu_{as}(CH_3)$ and $\nu_{as}(CH_2)$
2953 w	2950 m	2951 s	2956 w	2952 s	2953 vs	$\nu_{as}(CH_3)$ and $\nu_{as}(CH_2)$
2923 vw	2926 w	2924 w	2930 w	2925 m	2927 w	$\nu_{as}(CH_3)$ and $\nu_{as}(CH_2)$
2895 sh,w	2890 sh,m	2890 sh,w	2901 sh,w	2901 sh,m		$\nu_1(HCOO^-)$
2878 w	2876 vs	2872 vs	2885 w	2884 vs	2881 vs	$\nu_1(HCOO^-)$
2857 w			2859 w	2857 s	2867 vs	$\nu_1(HCOO^-)$
2824 w			2814 w	2814 vw		$\nu(NH_3)$
	2784 w	2786 vw		2784 vw	2786 w	Overtone
			2859 vw	2756 w	2754 w	Overtone
2747 vw	2747 w	2743 vw		2733 vw	2727 vw	Overtone
2715 vw	2739 vw		2723 vw	2712 vw		Overtone
2699 vw			2691 vw	2686 vw	2671 vw	Overtone
2655 vw			2658 vw			Overtone
2631 vw			2633 vw			Overtone

2504 vw			2502 vw			Overtone
	1669 m	1668 m		1679 w	1678 w	$\delta_{as}(NH_3)$ and $\nu_4(HCOO^-)$
1643 vs	1647 vw	1633 vw	1652 vs	1647 vw	1642 vw	$\delta_{as}(NH_3)$ and $\nu_4(HCOO^-)$
1627 sh,s	1625 vw		1634 sh,s	1625 vw	1621 vw	$\delta_{as}(NH_3)$ and $\nu_4(HCOO^-)$
			1612 s			$\delta_{as}(NH_3)$ and $\nu_4(HCOO^-)$
1596 vs	1591 vw	1591 vw	1589 sh,m	1588 vw	1591 w	$\nu_4(HCOO^-)$
1580 sh,m						$\nu_4(HCOO^-)$
1504 sh,vw			1500 sh,vw			$\delta_s(NH_3)$
1492 w			1486 w			$\delta_s(NH_3)$
1462 vw			1472 vw			$\delta(CH_3)$ and $\delta(CH_2)$
1459 vw	1457 w	1452 w	1459 vw	1456 w	1454 w	$\delta(CH_3)$ and $\delta(CH_2)$
1451 sh,vw	1447 w		1450 sh,vw	1449 w		$\delta(CH_3)$ and $\delta(CH_2)$
1399 w	1398 vw	1400 vw	1397 sh,w	1397 vw	1403 vw	$\nu_5(HCOO^-)$
1382 w	1380 s	1379 vs	1392 m			$\nu_5(HCOO^-)$
			1387 m	1384 m	1381 m	$\nu_5(HCOO^-)$
				1377 m	1347 m	$\nu_5(HCOO^-)$
	1336 m	1335 m		1367 w		$\nu_5(HCOO^-)$
	1326 w					$\nu_2(HCOO^-)$
1319 vs	1316 w	1314 w	1338 s			$\nu_2(HCOO^-)$
1306 sh,m		1311 w	1321 m	1319 w	1319 w	$\nu_2(HCOO^-)$
	1286 w	1279 w	1308 m			$\nu_2(HCOO^-)$
1273 m	1272 vw		1295 m	1291 vw	1287 vw	$\nu_2(HCOO^-)$ and $\rho(CH_2)$
1228 w	1227 vw	1225 vw	1229 w	1226 vw	1224 vw	$\rho(CH_3)$
1211 vw			1211 w	1208 vw	1206 vw	$\rho(CH_3)$
1059 sh,vw	1056 w	1057 w		1070 sh,w		$\nu_6(HCOO^-)$ and $\nu_{as}(CCN)$
1049 w	1045 vw	1046 vw	1055 sh,vw	1056 w	1055 w	$\nu_6(HCOO^-)$ and $\nu_{as}(CCN)$

			1050 w	1044 vw		$\nu_6(HCOO^-)$ and $\nu_{as}(CCN)$
1012 w	1010 vw	1004 vw	1013 w	1011 vw		$\rho(NH_3)$
999 vw	997 vw		998 vw	995 vw	996 vw	$\rho(NH_3)$
	874 w	873 w		874 w	872 w	$\nu_s(CCN)$
815 m			823 m			$\nu_3(HCOO^-)$
	803 w	802 w	814 m	803 w	801 w	$\nu_3(HCOO^-)$
793 w	790 w	791 w	792 w	788 w	789 w	$\nu_3(HCOO^-)$
413 s			455 s			T'(M^{III}) and T'($HCOO^-$)
	414 vw	417 vw		424 w		$\delta(CCN)$
	339 w	337 w		335 w	334 w	T'(Na^+)
277 w			313 w	303 w	296 w	T'(M^{III}), T'($HCOO^-$) and T'(Na^+)
				285 w	283 w	T'($HCOO^-$), T'(Na^+) and T'(M^{III})
242 w	242 w	240 w	253 w			T'($HCOO^-$), T'(Na^+) and T'(M^{III})
222 w	217 w		229 w	225 w		T'($HCOO^-$)
190 m			202 m			T'($HCOO^-$)
	185 m	181 m		192 w	180 m	L($HCOO^-$)
	160 m	149 m	174 m	160 m	154 m	L($HCOO^-$)
141 vw			146 sh,vw	143 m		L($HCOO^-$)
	121 m	110 m		129 m	123 m	L($HCOO^-$)
108 vw	108 m		116 w	101 m		L($HCOO^-$)
	85 m	72 m		86 m	78 w	T(EtA^+), L(EtA^+)
	69 m			68 m	59 m	T(EtA^+), L(EtA^+)
	57 m			56 w		T(EtA^+), L(EtA^+)

[a]Key: RT – room temperature; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad; ν, stretching vibration; ν_s, symmetric stretching vibration; ν_{as}, antisymmetric stretching vibration; δ, bending vibration; δ_s, bending symmetric vibration; δ_{as}, bending antisymmetric stretching; ρ, rocking vibration; T', translation; L, libration and $\nu_1 - \nu_5$, characteristic vibrations of $HCOO^-$ ion.[17] SE = ±0.1 cm^{-1}.

Table S5. The comparison of distortion parameters together with the sum of standard errors for heterometallic MOFs of general formula $[A][Na_{0.5}M^{III}_{0.5}(HCOO)_3]$, where A is ammonium cation, DMA (dimethylammonium) or EtA (ethylammonium) and M^{III} = Cr, Fe and Al in high temperature (HT) and low temperature (LT) phases.

		EtANaCr	**EtANaAl**	EtANaFe[17]	DMANaCr[16]	DMANaFe[15]
HT	$M^{III}O_6$	8.98 ± 0.96˚	7.43 ± 1.08˚	9.24˚	9.60˚	10.54˚
	NaO_6	28.4 ± 0.97˚	29.21 ± 1.32˚	23.8˚	9.96˚	6.96˚
LT	$M^{III}O_6$	10.96 ± 0.59˚	9.35 ± 2.22˚	11.71˚		67.21˚
	NaO_6	34.95 ± 0.76˚	39.27 ± 2.09˚	32.5˚		62.07˚

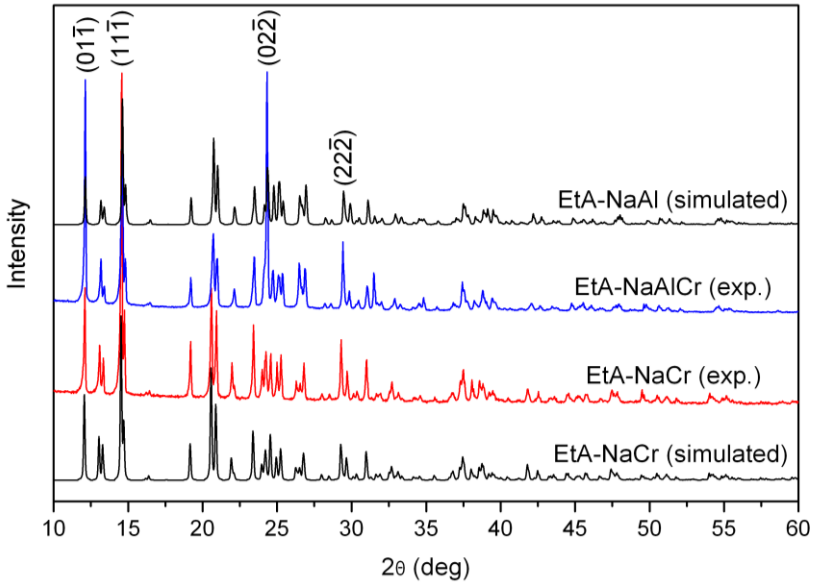

Figure S1. Powder XRD patterns for the as-prepared bulk samples of EtANaCr and EtANaAlCr together with the simulated ones based on the single crystal structures at 297 K (for EtANaCr) and at 270 K (for EtANaAl)

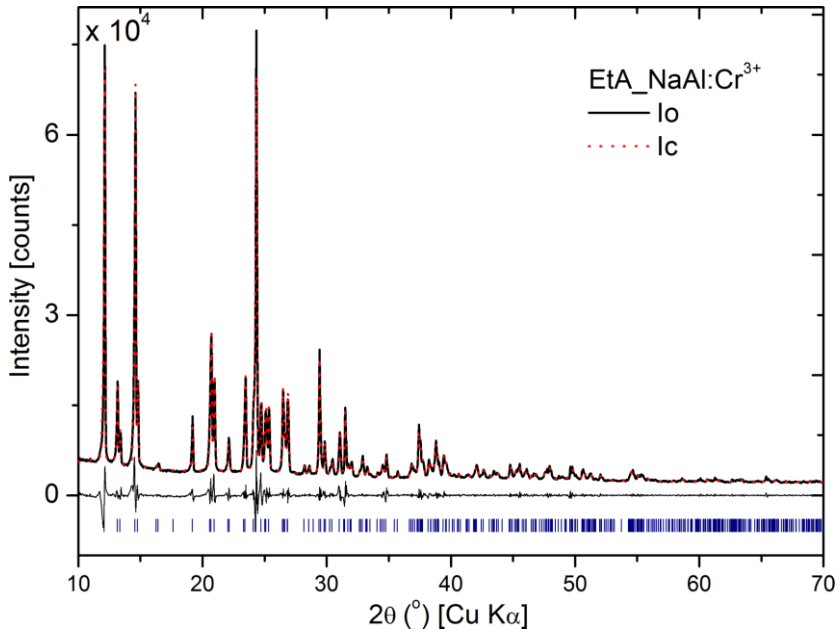

Figure S2. Le Bail fit of the EtANaAlCr powder diagram. The refined lattice parameters: a=8.060(1) Å b=9.255(1) Å, c=11.986(1) Å, β=90.94(1)°, V= 894.0(2) Å^3 crystal system monoclinic, space group *Pn*. The final agreement R factors for the profile: R_p: 0.043; wR_p=0.056; I_o and I_c denote observed and calculated intensities, respectively. The residuals are given at the bottom.

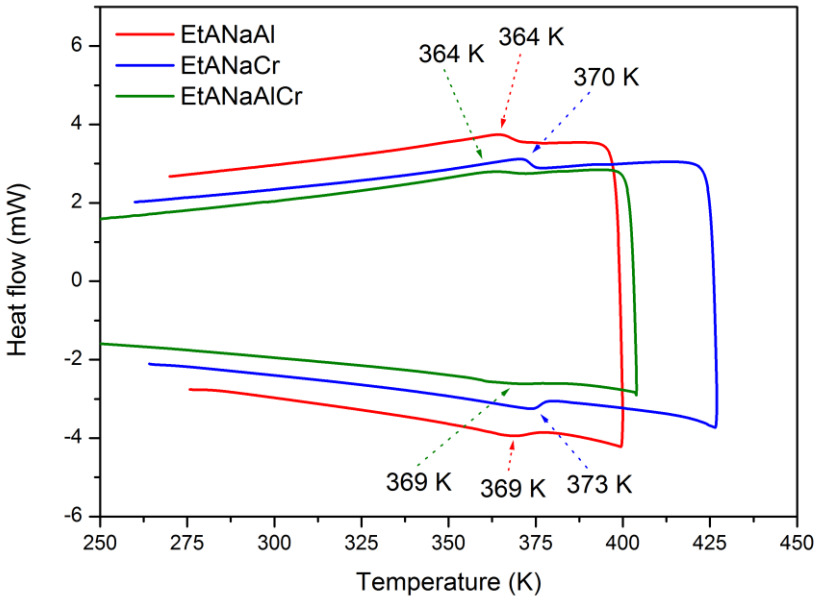

Figure S3. The DSC traces measured for EtANaCr (blue line), EtANaAl (red line) and EtANaCrAl (green line).

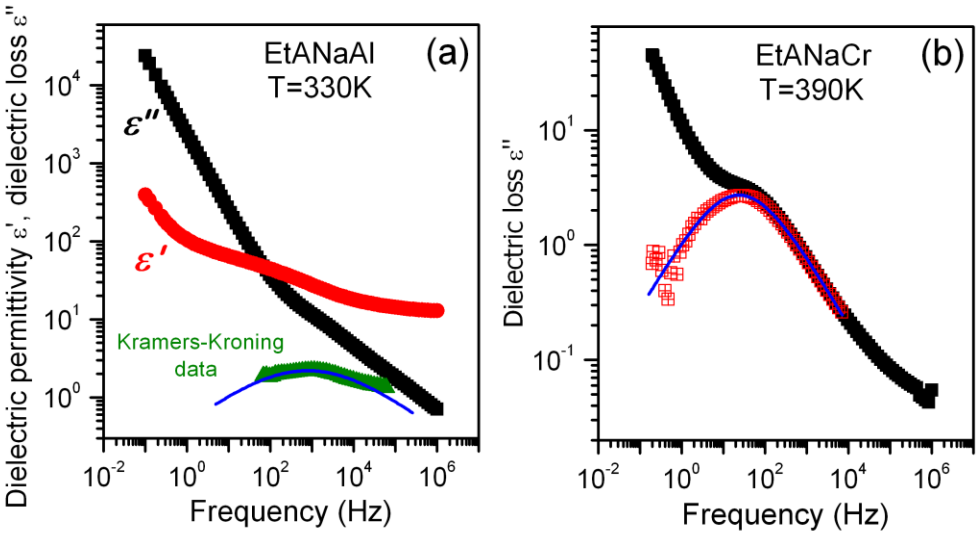

Figure S4 (a) The comparison of the ε”(f), ε’(f) and derivative data after Kramers-Kronig transformation for EtANaAl measured at 330 K. Solid curve is only the guide for the eyes. (b) The representative loss spectrum of EtANaCr measured at 390 K with and after subtraction of conductivity part. Solid curve depict Cole-Cole fitting function. Uncertainties are smaller than size of the symbols.

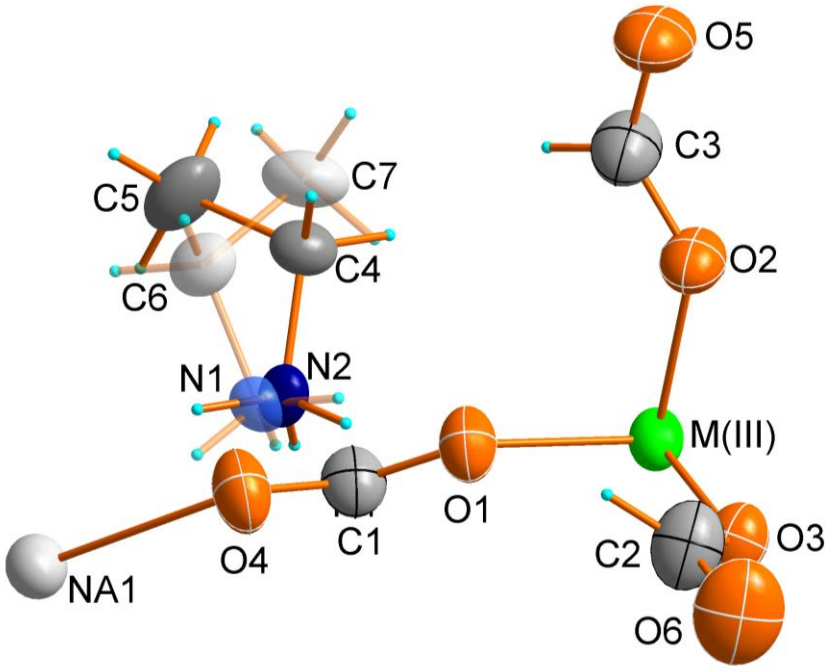

Figure S5. The content of the asymmetric unit in the high temperature phase of EtANaM^{III} formates. The EtA^{+} is disordered over two symmetrically independent positions. Both are occupied with ~50% probability.

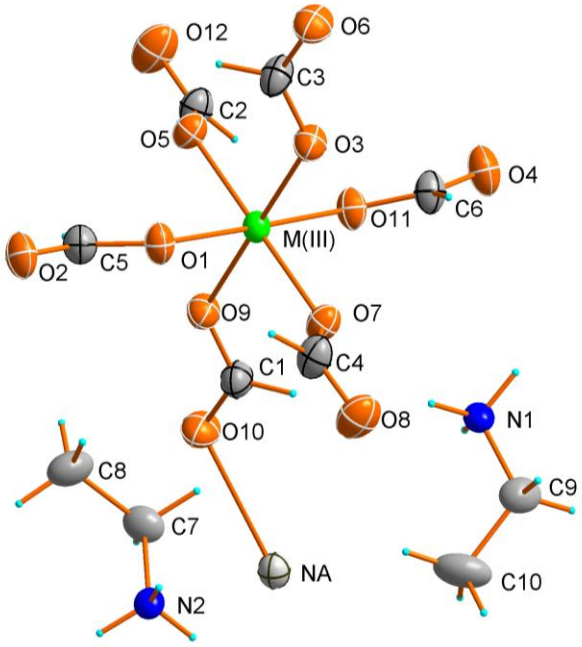

Figure S6. The content of the asymmetric unit in the polar phase *Pn* of EtANaM^{III} formates. The displacement ellipsoids are taken form the *Pn* phase of EtANaCr formate, T=297K.

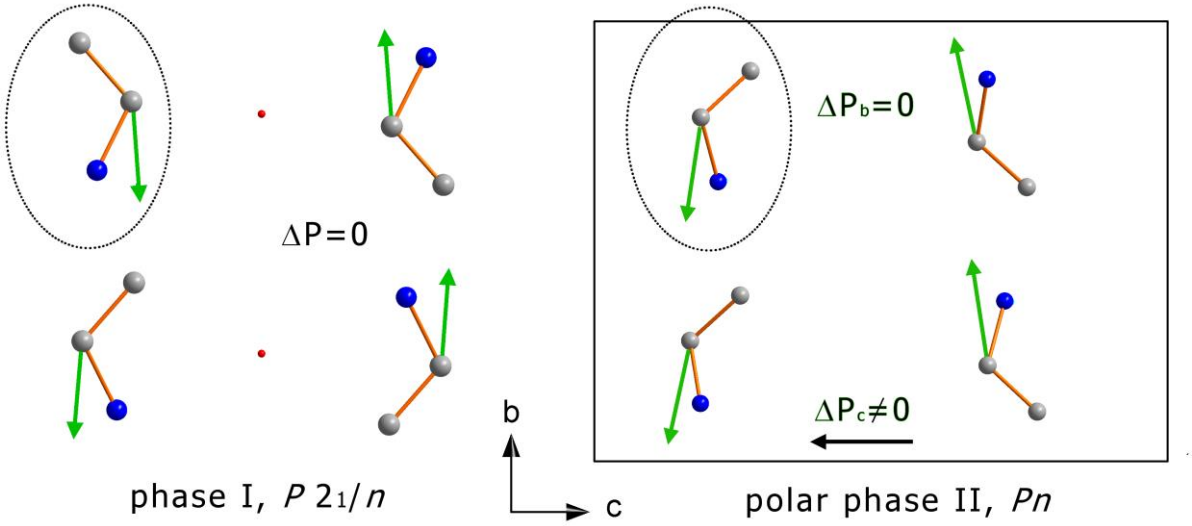

Figure S7. Every EtA^+ cation has an internal dipole moment represented by the green arrow. The resultant dipole moment from all EtA^+ in phase I is equal to zero due to the presence of the symmetry center (red dot). In the polar phase II, non-compensated EtA^+ dipoles give rise to the spontaneous polarization that occurs perpendicularly to *b* direction in (*a*,*c*) plane. For the picture clarity only one of the two possible orientations of EtA^+inphase I has been drawn.

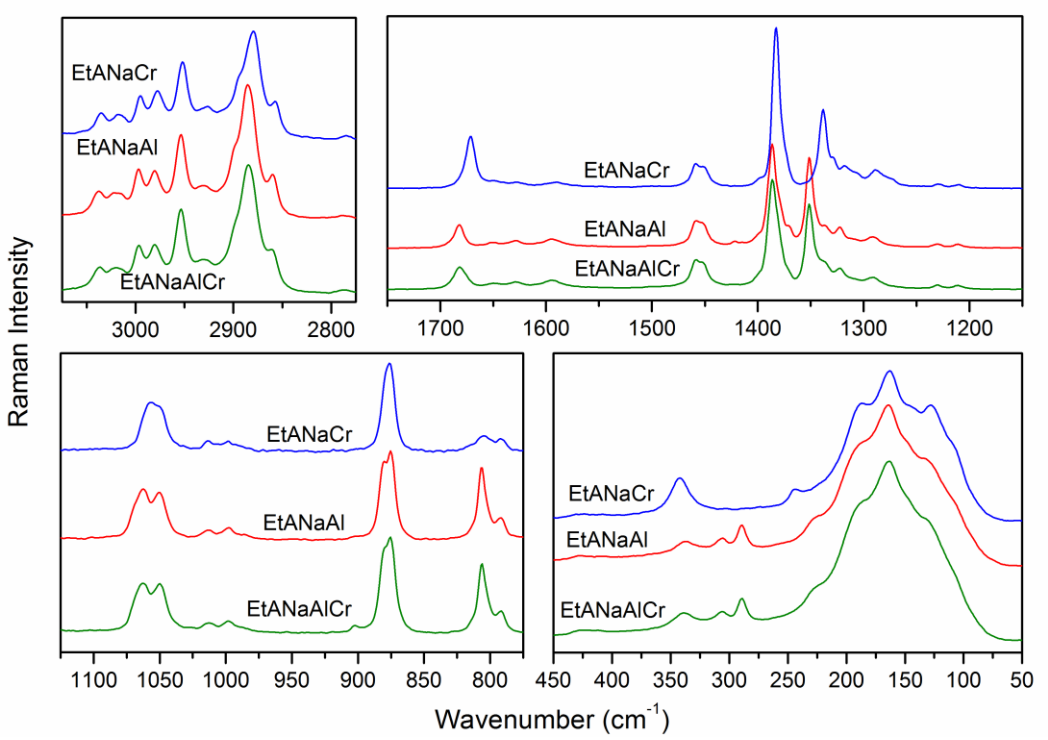

Figure S8. The details of Raman spectra of EtANaCr and EtANaAlCr.

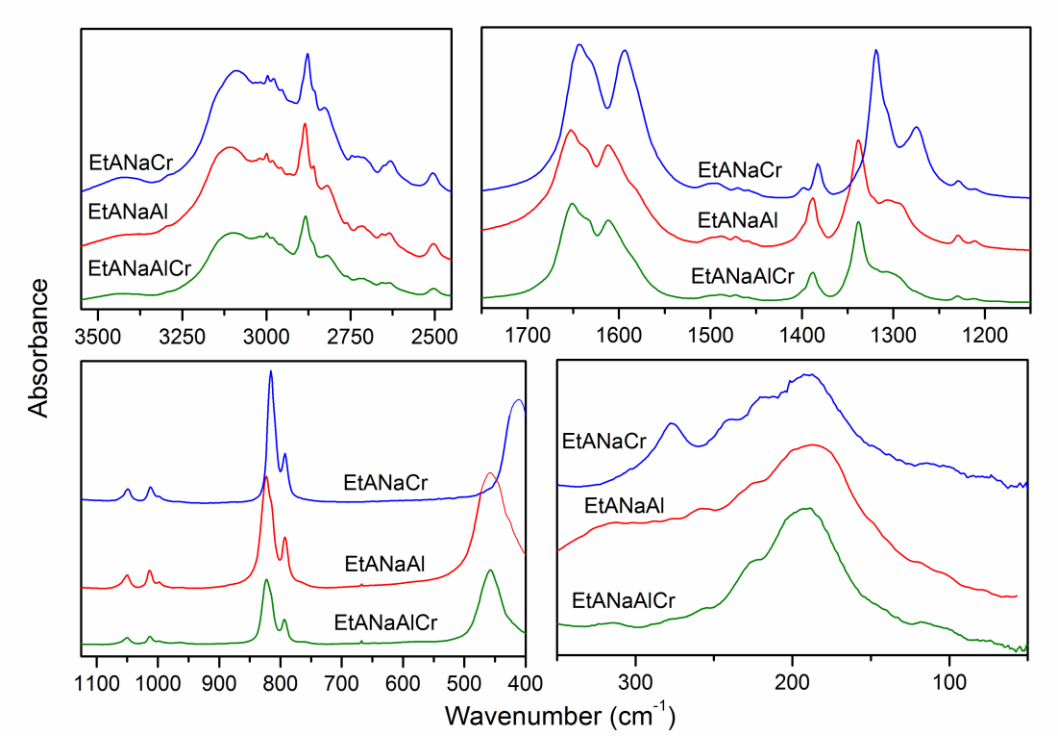

Figure S9. The details of IR spectra of EtANaCr and EtANaAlCr.

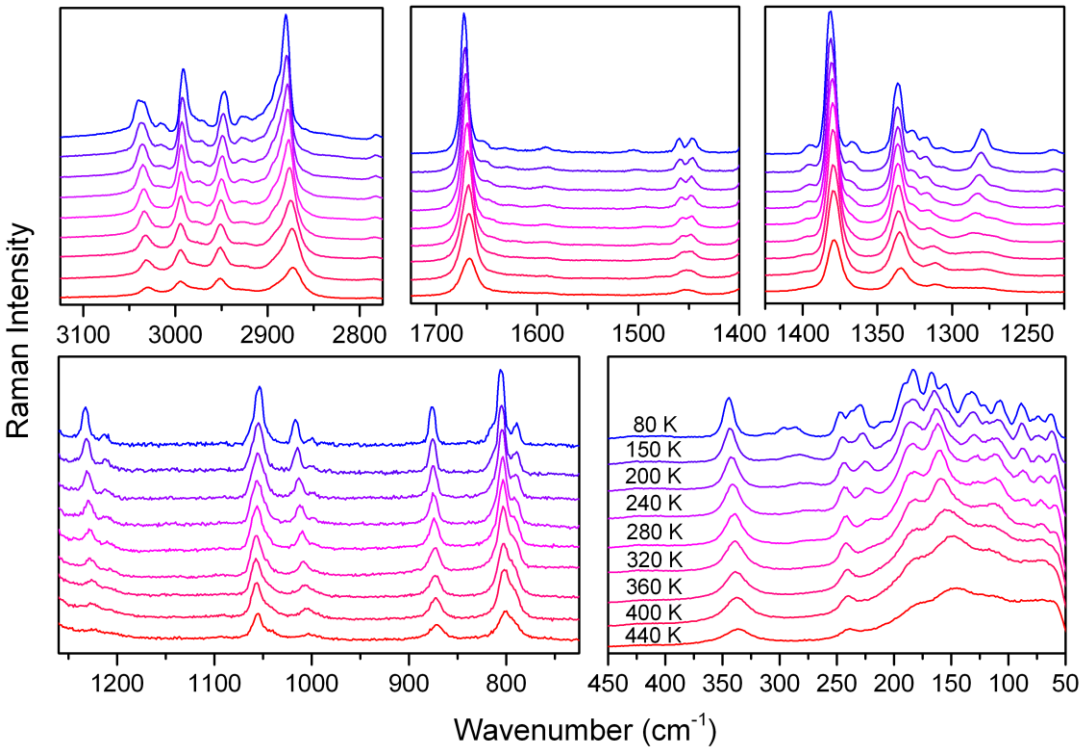

Figure S10. Temperature-dependent Raman spectra of EtANaCr.

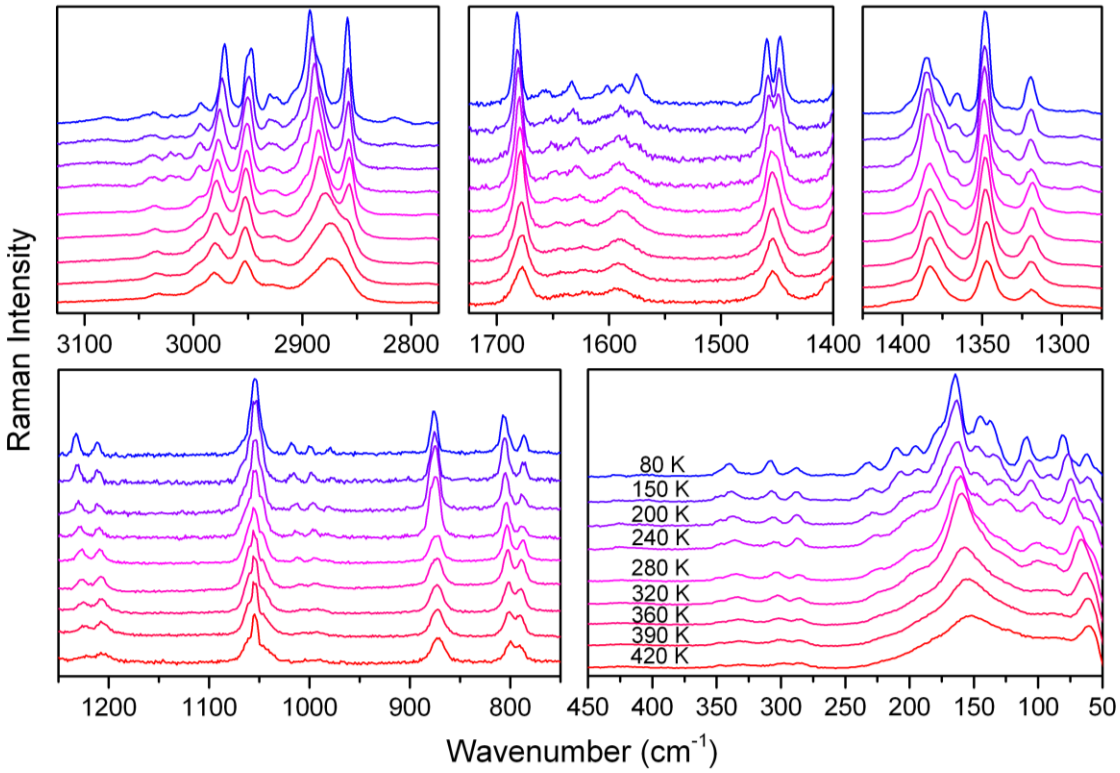

Figure S11. Temperature-dependent Raman spectra of EtANaAlCr.

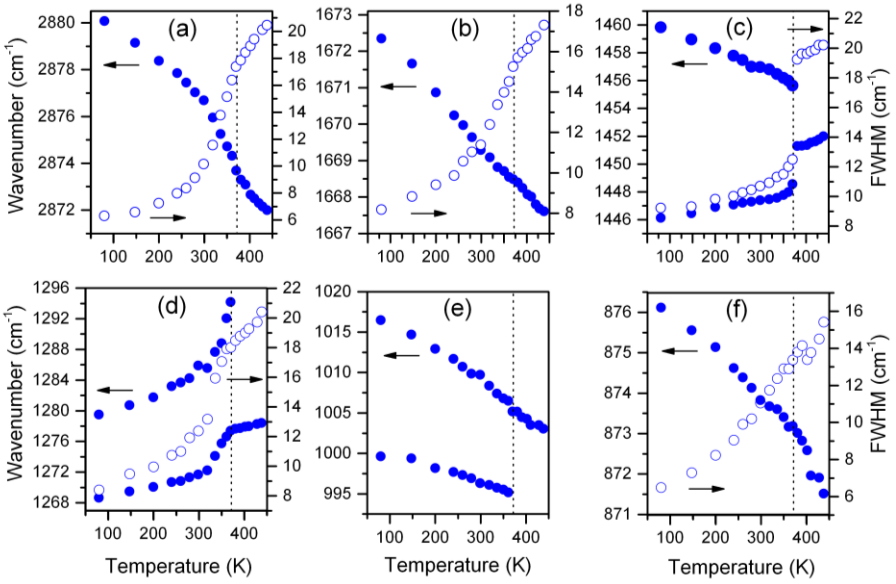

Figure S12. The temperature depencies of wavenumbers (full circles, left axes) and FWHM (open circles, right axes) in cm^{-1} of $\nu_1(HCOO^-)$ (a), $\nu_4(HCOO^-)$ (b), $\delta(CH_3)$ and $\delta(CH_2)$ (c), $\rho(CH_3)$ (d), $\rho(NH_3)$ (e) and $\nu_s(CCN)$ (f) vibrations for EtANaCr. Dotted line indicates the phase transition temperature. Uncertainties in phonon wavenumbers are smaller than size of the symbols.

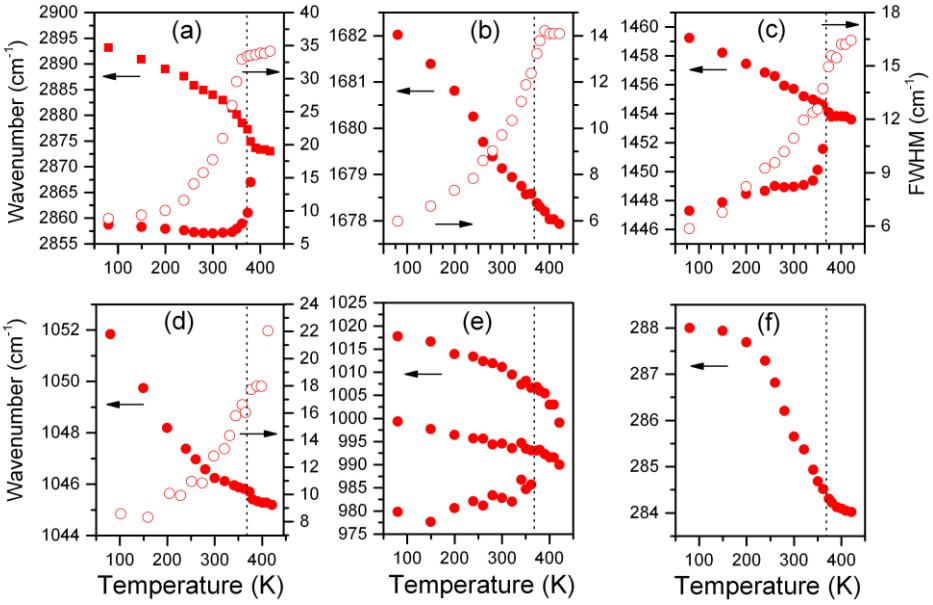

Figure S13. The temperature depencies of wavenumbers (full circles, left axes) and FWHM (open circles, right axes) in cm^{-1} of $\nu_1(HCOO^-)$ (a), $\nu_4(HCOO^-)$ (b), $\delta(CH_3)$ and $\delta(CH_2)$ (c), $\nu_6(HCOO^-) + \nu_{as}(CCN)$ (d), $\rho(NH_3)$ (e) and strongly coupled translational $T'(HCOO^-) + T'(Na^+)$

+ T'(Al^{3+}/Cr^{3+}) (f) vibrations for EtANaAlCr. Dotted line indicates the phase transition temperature. Uncertainties in phonon wavenumbers are smaller than size of the symbols.

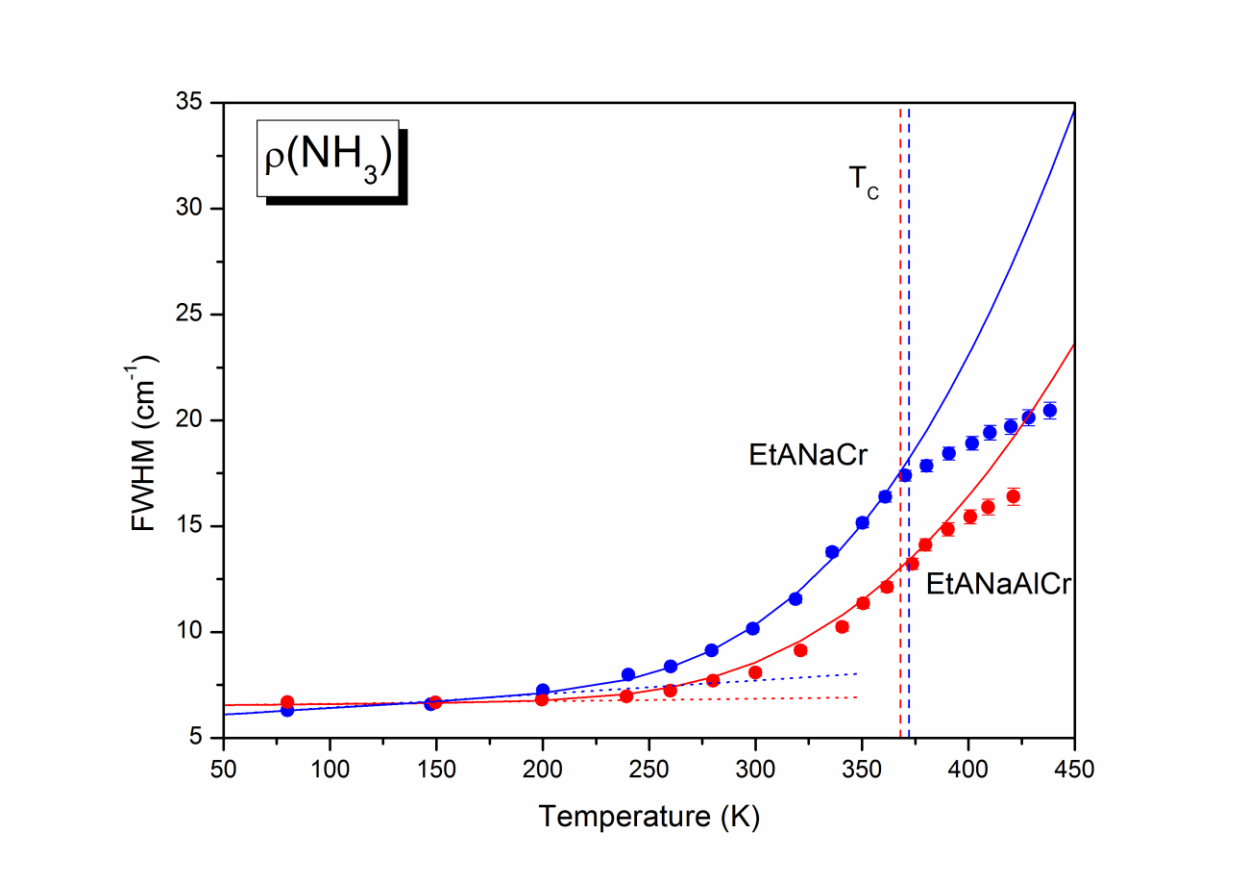

Figure S14. Temperature behaviour of FWHM of the $\rho(NH_3^+)$ Raman bands at 1010 cm^{-1} (wavenumber at 300 K) for EtANaCr (blue circles) and at 1011 cm^{-1} (wavenumber at 300 K) EtANaAlCr (red circles) together with error bars. Solid lines show fit on the data to eq. 1. The dotted lines represent the contribution due to reorientational processes and dashed lines show the phase transitions temperatures.