Electronic Supplementary Information
for

Mechanism of isosymmetric polar order-disorder phase transition in pyroelectric $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$ double perovskite

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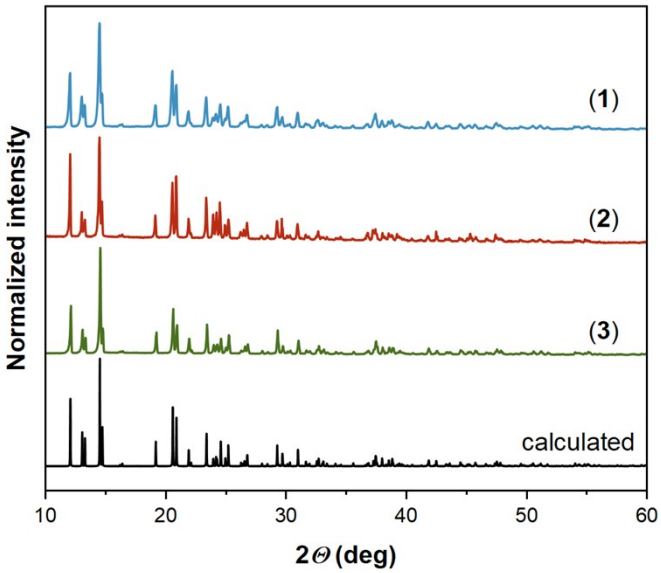


Fig. S1. Powder XRD patterns of (**1**), (**2**), and (**3**) compared to the simulated pattern based on the single crystal data obtained for (1) at 293 K; (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$; (**2**), $[CH_3CH_2NH_3]_2NaGa_{0.069}Cr_{0.931}(HCOO)_6$; (**3**), $[CH_3CH_2NH_3]_2NaGa_{0.99}Fe_{0.01}(HCOO)_6$;

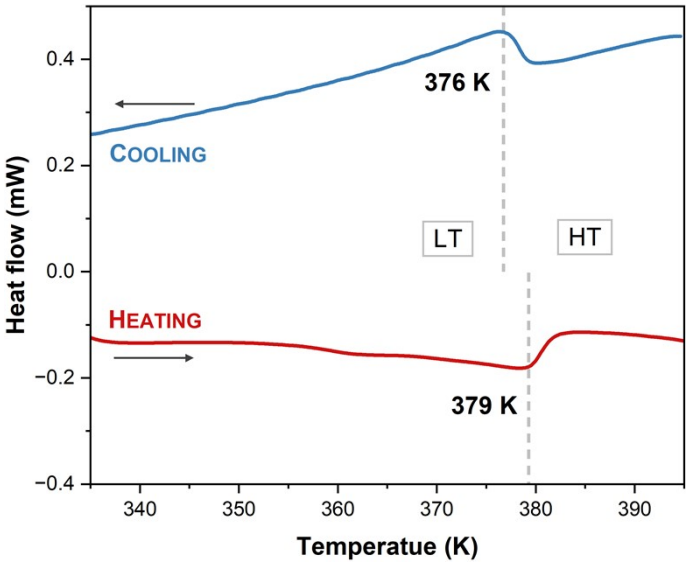
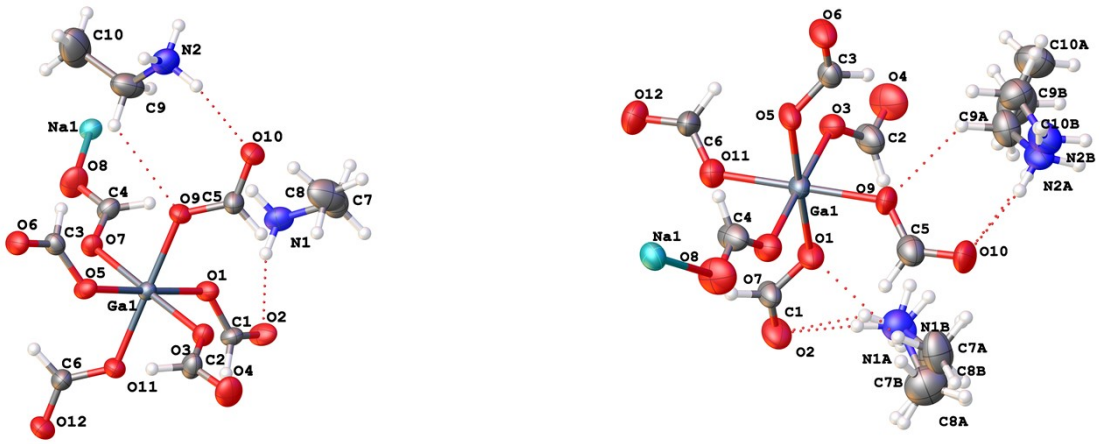
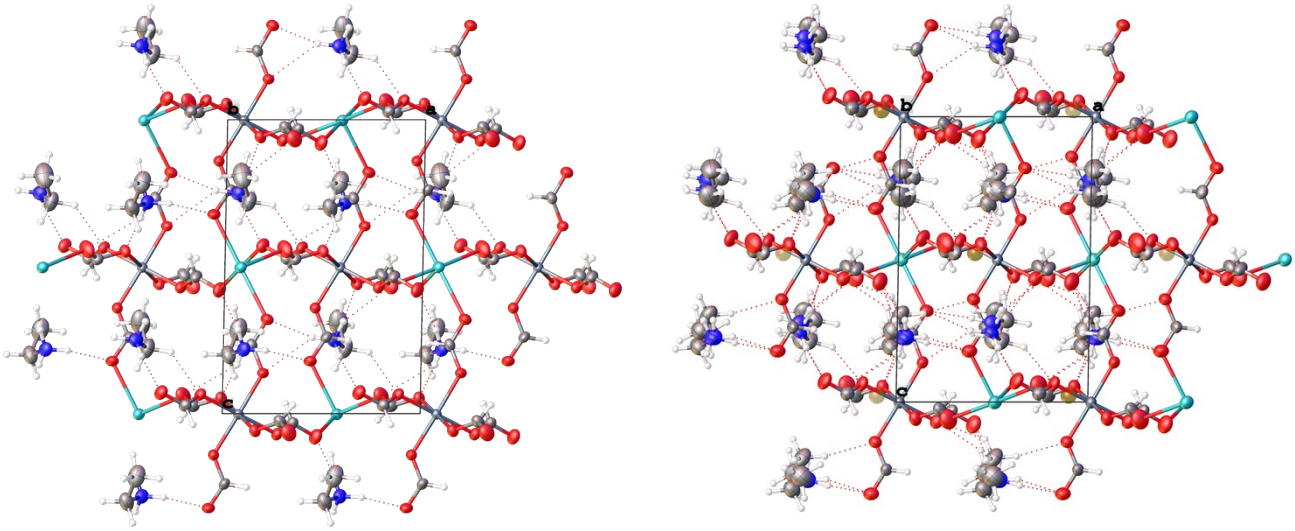


Fig. S2. The DSC curve recorded for (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$.



(a) (b)

Fig. S3. Asymmetric part of unit cell for (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$, at (a) 293 K and (b) 391 K. Displacement ellipsoids are drawn at the 50% probability level.



(a) (b)

Fig. S4. Packing diagrams along the *b* axis for (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$, at (a) 293 K and (b) 391 K. Displacement ellipsoids are drawn at the 50% probability level.

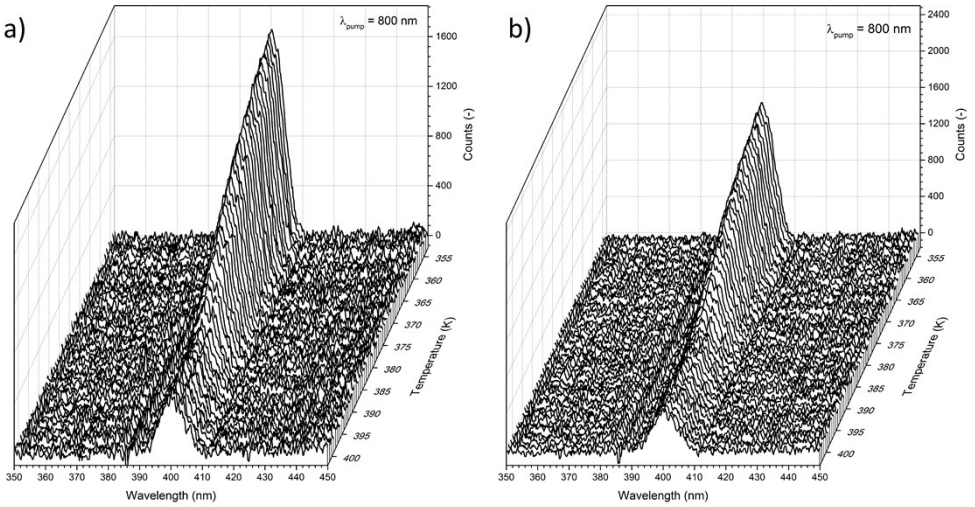


Fig. S5. SHG traces collected for (1) during (a) heating run, and (b) cooling run.

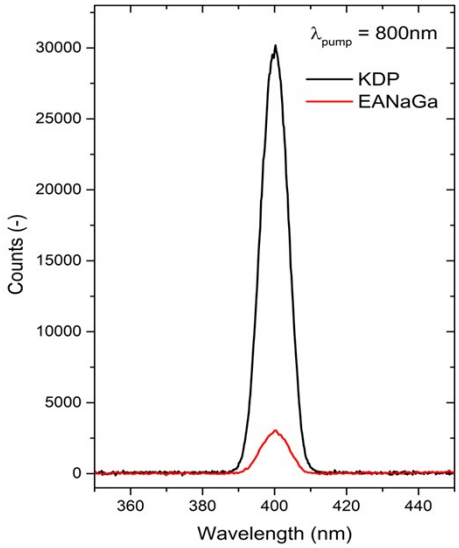


Fig. S6. Overlay of SHG traces obtained for (1) and KDP. Note that signal collection times were 6000 ms and 500 ms for (1) and KDP, respectively. Relative SHG efficiency of (1) is about 0.01 that of KDP.

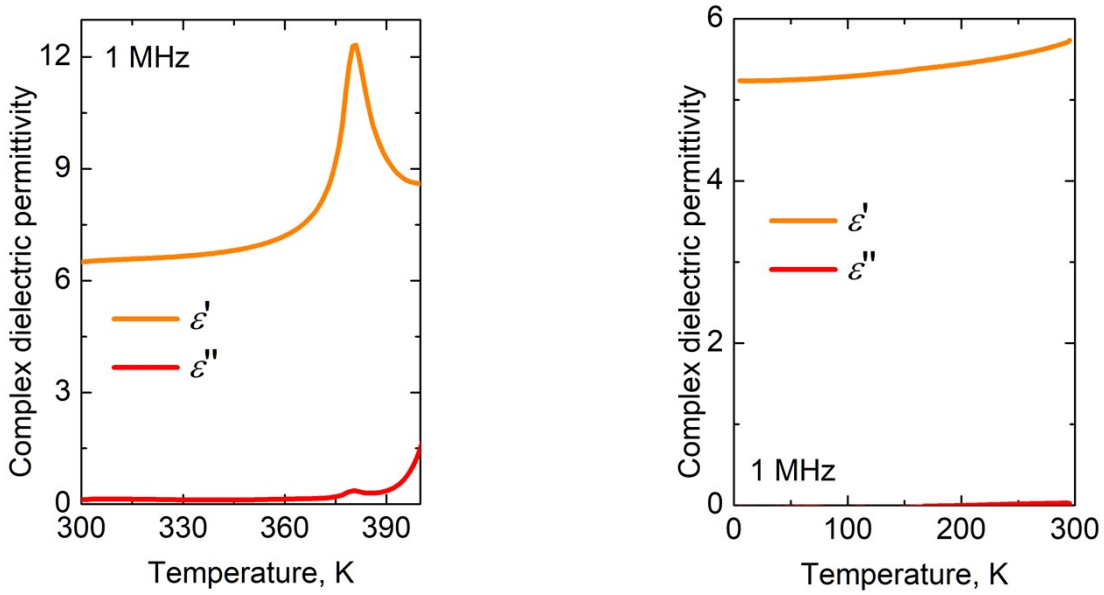


Fig. S7. Temperature dependence of the complex dielectric permittivity of pellet sample (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$, measured at 1 MHz above (a) and below RT (b). A clear phase transition anomaly can be observed at 380 K (a).

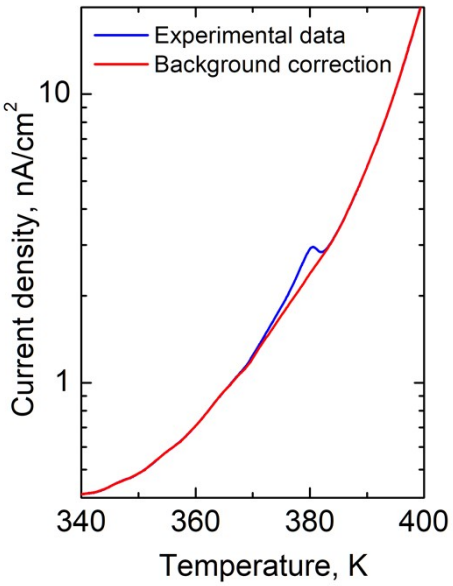


Fig. S8. Temperature dependence of the thermally stimulated current of the pellet sample (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$, prior the background correction. The red curve indicates the background correction employed to extract the pyrocurrent due to the phase transition.

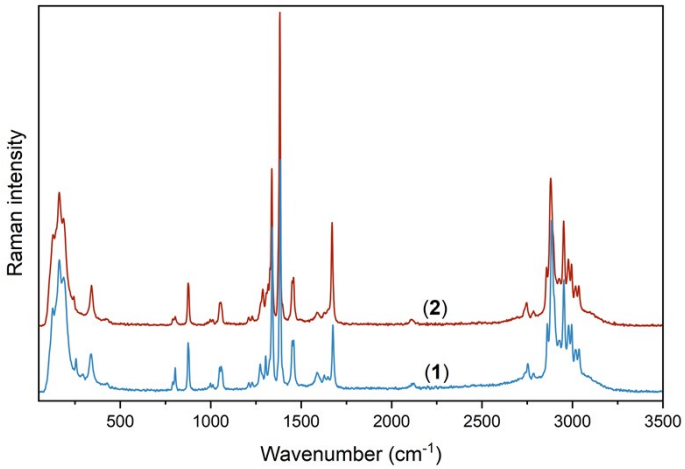


Fig. S9. Comparison of RT Raman spectra of (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$ and (**2**), $[CH_3CH_2NH_3]_2NaGa_{0.069}Cr_{0.931}(HCOO)_6$.

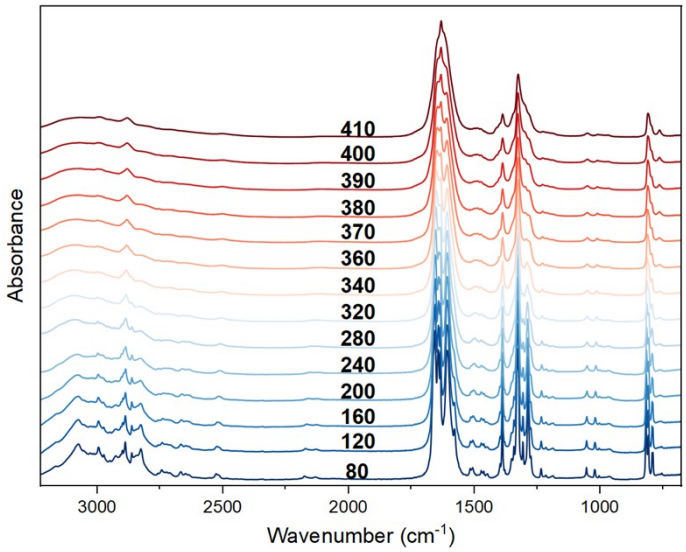


Fig. S10. Temperature-dependent IR spectra of (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$.

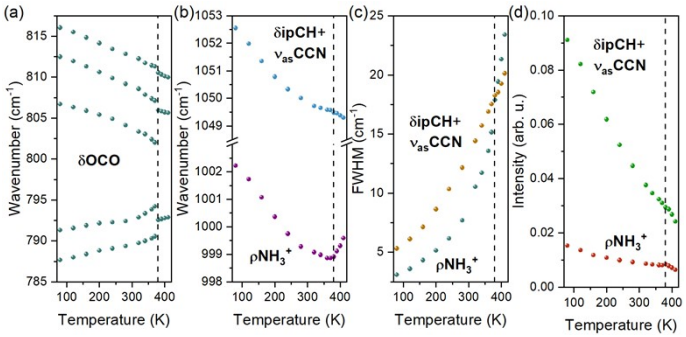


Fig. S11. Thermal evolution of selected IR bands for (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$.

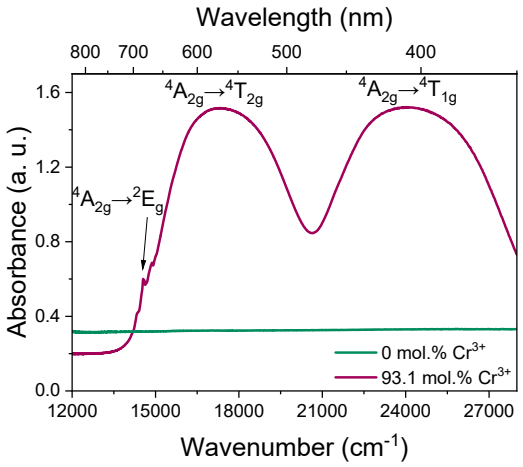


Fig. S12. Room temperature absorption spectra of (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$ and (**2**), $[CH_3CH_2NH_3]_2NaGa_{0.069}Cr_{0.931}(HCOO)_6$.

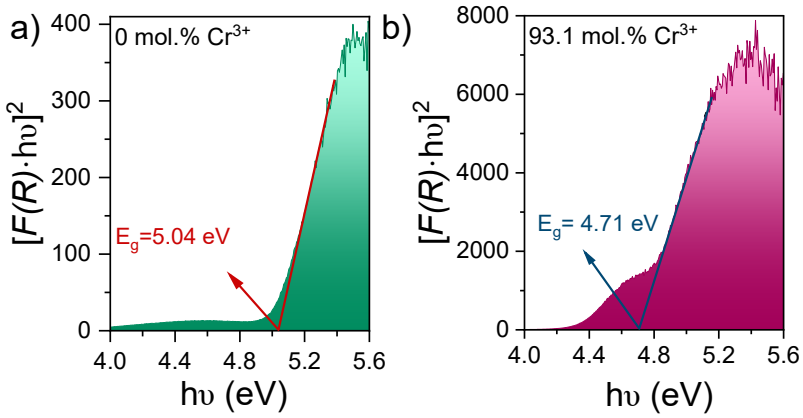


Fig. S13. Energy band gap of investigated samples estimated by x-axis intersection point of the linear fit of the Tauc plot. Using the diffuse reflectance spectrum, it is possible to determine the energy band gap (E_g) of investigated samples by applying the Kubelka-Munk relation (Z. Technol. Phys. 1931, 12, 593−599): $F(R) = (1 - R)^2 / 2R$, where R is reflectance. The modification of this method proposed by Tauc in 1966 (Status Solidi B 1966, 15, 627−637) assumed that the E_g can be determined based on the graphical examination of the following function: $[F(R \cdot hv]^n = B(hv - E_g)$, where h denotes the Planck constant, v is the photon's frequency, and B is a constant. The n factor is related to the type of electron transition and takes a 1/2 or 2 value for the direct and indirect transition band gaps, respectively (J. Sol-Gel Sci. Technol. 2012, 61, 1–7, *J. Phys. Chem. Lett*. 2018, 9, 23, 6814–6817).

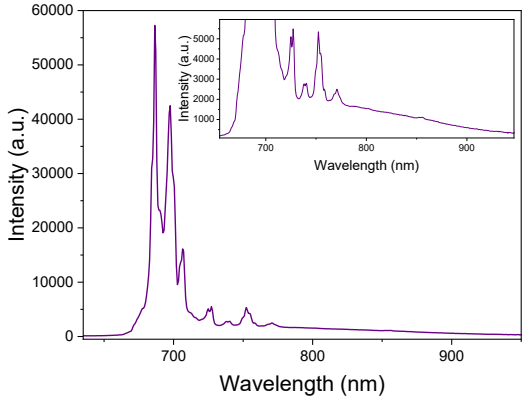


Fig. S14. The low-temperature (80 K) emission spectrum of (**2**), $[EA]_2NaCr_{0.931}Ga_{0.069}(HCOO)_6$, in the inset magnification of the spectrum, shows the broad emission from the $^4T_{2g}$ emission level.

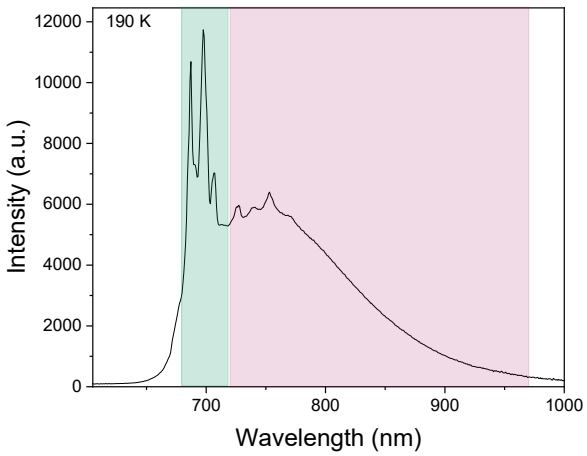


Fig. S15. The emission spectra of (**2**), $[EA]_2NaCr_{0.931}Ga_{0.069}(HCOO)_6$, at 190 K presented spectral ranges used to determine FIR.

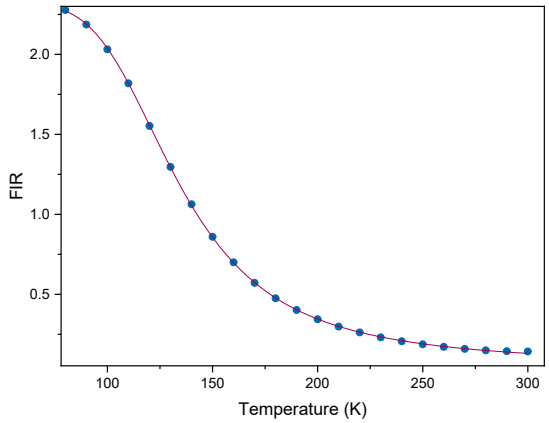


Fig. S16. Changes of FIR ratio with the temperature of (**2**), $[EA]_2NaCr_{0.931}Ga_{0.069}(HCOO)_6$.

Tab. S1. Experimental data for (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$, at 293 and 391 K.

Crystal data		
Chemical formula	$(C_2H_5NH_3)_2GaNa(HCOO)_6$ (**1**)	
M_r	455.00	
Crystal system, space group	Monoclinic, *Pn*	
Temperature (K)	293(2)	391(2)
***a*, *b*, *c* (Å)**	8.1127 (5), 9.2570 (6), 12.0281 (8)	8.1080 (6), 9.3326 (7), 12.0697 (10)
α, β, γ (°)	90.000 (0), 91.084 (5), 90.000 (0)	90.000, 90.940 (7), 90.000
***V* (Å^3)**	903.14 (10)	913.18 (12)
Z	2	
Radiation type	Mo *K*α	
***μ* (mm^{-1})**	1.61	1.59
Crystal size (mm)	0.30 x 0.20 x 0.10	
Data collection		
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6130, 3505, 3362	4249, 2831, 2678
R_{int}	0.019	0.025
(sin θ/λ$_{max}$ (Å^{-1})	0.651	0.617
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.025, 0.056, 1.05	0.034, 0.083, 1.08
No. of reflections	3505	2831
No. of parameters	241	292
Δρ$_{max}$, Δρ$_{min}$ (e Å^{-3})	0.29, −0.27	0.34, −0.37

Tab. S2. Comparison of thermal and structural parameters for $[EA]_2NaM^{III}(HCOO)_6$ double perovskites.

M^{III}	T_C (K) [a]	ΔS (Jmol^{-1}K^{-1}) [b]	σ^2 (deg^2) [c]		Δ × 10^2 [d]	
			NaO_6	$M^{III}O_6$	NaO_6	$M^{III}O_6$
Ga^{3+} (1)	379/376	3.7	17.04 [e] / 12.06 [f]	1.77 [e] / 1.43 [f]	1.96 [e] / 2.31 [f]	0.40 [e] / 0.27 [f]
Al^{3+}	369/364	2.0	18.03 [g] / 7.99 [h]	0.91 [g] / 0.47 [h]	1.82 [g] / 1.96 [h]	0.37 [g] / 0.25 [h]
Cr^{3+}	373/370	4.0	14.94 [i] / 7.33 [j]	1.16 [i] / 0.73 [j]	1.88 [i] / 2.19 [j]	0.20 [i] / 0.09 [j]
Fe^{3+}	361/359	5.0	12.84 [i] / 5.06 [k]	1.50 [i] / 0.65 [k]	1.72 [i] / 1.92 [k]	0.33 [i] / 0.16 [k]

[a] heating/cooling; [b] estimated for the $[EA]_2NaM^{III}(HCOO)_6$ (Z = 2) formula; [c] bond angle variance for HT/LT phase; [d] distortion index for HT/LT phase; [e] 293 K; [f] 391 K; [g] 270 K; [h] 375 K; [i] 297 K; [j] 400 K; [k] 377 K. Literature data for M^{III} = Al^{3+}, Cr^{3+}, and Fe^{3+} were taken from: 10.1039/C6CP05151K and 10.1039/C5DT04536C. The bond angle variance and distortion indexes were calculated using Vesta software (10.1107/S0021889808012016).

Tab. S3. Selected geometric parameters (Å, °) for (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$, at 293 and 391 K.

293 K			
Ga1—O1	1.966 (4)	O12—C6	1.238 (5)
Ga1—O3	1.964 (2)	C1—H1	0.9300
Ga1—O5	1.971 (3)	C2—H2	0.9300
Ga1—O7	1.985 (2)	C3—H3	0.9300
Ga1—O9	1.987 (3)	C4—H4	0.9300
Ga1—O11	1.977 (2)	C5—H5	0.9300
Na1—O2^{i}	2.437 (5)	C6—H6	0.9300
Na1—O4^{ii}	2.418 (4)	N1—H1A	0.8900
Na1—O6^{iii}	2.441 (5)	N1—H1B	0.8900
Na1—O8	2.385 (4)	N1—H1C	0.8900
Na1—O10^{iv}	2.526 (3)	N1—C7	1.470 (6)
Na1—O12^{v}	2.531 (3)	C7—H7A	0.9700
O1—C1	1.275 (7)	C7—H7B	0.9700
O2—Na1^{vi}	2.437 (5)	C7—C8	1.490 (7)
O2—C1	1.228 (7)	C8—H8A	0.9600
O3—C2	1.274 (5)	C8—H8B	0.9600
O4—Na1^{vii}	2.418 (4)	C8—H8C	0.9600
O4—C2	1.215 (5)	N2—H2A	0.8900
O5—C3	1.261 (7)	N2—H2B	0.8900
O6—Na1^{viii}	2.441 (5)	N2—H2C	0.8900
O6—C3	1.220 (7)	N2—C9	1.468 (6)
O7—C4	1.289 (5)	C9—H9A	0.9700
O8—C4	1.215 (5)	C9—H9B	0.9700
O9—C5	1.268 (5)	C9—C10	1.466 (8)
O10—Na1^{ix}	2.526 (3)	C10—H10A	0.9600
O10—C5	1.234 (5)	C10—H10B	0.9600
O11—C6	1.256 (5)	C10—H10C	0.9600
O12—Na1^{x}	2.531 (3)		
O1—Ga1—O5	178.28 (16)	O5—C3—H3	117.3
O1—Ga1—O7	89.94 (12)	O6—C3—O5	125.5 (5)
O1—Ga1—O9	88.93 (13)	O6—C3—H3	117.3
O1—Ga1—O11	91.12 (13)	O7—C4—H4	118.2
O3—Ga1—O1	89.18 (12)	O8—C4—O7	123.6 (4)
O3—Ga1—O5	92.49 (12)	O8—C4—H4	118.2
O3—Ga1—O7	178.87 (12)	O9—C5—H5	117.5
O3—Ga1—O9	90.64 (11)	O10—C5—O9	125.0 (4)
O3—Ga1—O11	88.89 (11)	O10—C5—H5	117.5
O5—Ga1—O7	88.38 (11)	O11—C6—H6	116.7
O5—Ga1—O9	90.66 (13)	O12—C6—O11	126.6 (4)
O5—Ga1—O11	89.30 (13)	O12—C6—H6	116.7
O7—Ga1—O9	88.63 (11)	H1A—N1—H1B	109.5
O11—Ga1—O7	91.85 (11)	H1A—N1—H1C	109.5
O11—Ga1—O9	179.53 (12)	H1B—N1—H1C	109.5
O2^{i}—Na1—O6^{iii}	171.68 (14)	C7—N1—H1A	109.5
O2^{i}—Na1—O10^{iv}	84.11 (13)	C7—N1—H1B	109.5
O2^{i}—Na1—O12^{v}	96.89 (13)	C7—N1—H1C	109.5
O4^{ii}—Na1—O2^{i}	86.61 (15)	N1—C7—H7A	109.4
O4^{ii}—Na1—O6^{iii}	89.65 (15)	N1—C7—H7B	109.4
O4^{ii}—Na1—O10^{iv}	89.02 (10)	N1—C7—C8	111.3 (4)
O4^{ii}—Na1—O12^{v}	91.69 (14)	H7A—C7—H7B	108.0
O6^{iii}—Na1—O10^{iv}	88.40 (12)	C8—C7—H7A	109.4

O6^{iii}—Na1—O12^{v}	90.64 (14)	C8—C7—H7B	109.4
O8—Na1—O2^{i}	91.58 (15)	C7—C8—H8A	109.5
O8—Na1—O4^{ii}	174.61 (15)	C7—C8—H8B	109.5
O8—Na1—O6^{iii}	92.79 (16)	C7—C8—H8C	109.5
O8—Na1—O10^{iv}	95.85 (15)	H8A—C8—H8B	109.5
O8—Na1—O12^{v}	83.48 (11)	H8A—C8—H8C	109.5
O10^{iv}—Na1—O12^{v}	178.80 (19)	H8B—C8—H8C	109.5
C1—O1—Ga1	127.3 (4)	H2A—N2—H2B	109.5
C1—O2—Na1^{vi}	117.3 (4)	H2A—N2—H2C	109.5
C2—O3—Ga1	128.3 (3)	H2B—N2—H2C	109.5
C2—O4—Na1^{vii}	123.5 (3)	C9—N2—H2A	109.5
C3—O5—Ga1	126.0 (4)	C9—N2—H2B	109.5
C3—O6—Na1^{viii}	119.7 (3)	C9—N2—H2C	109.5
C4—O7—Ga1	124.6 (3)	N2—C9—H9A	109.3
C4—O8—Na1	130.5 (3)	N2—C9—H9B	109.3
C5—O9—Ga1	127.2 (3)	H9A—C9—H9B	107.9
C5—O10—Na1^{ix}	120.0 (3)	C10—C9—N2	111.7 (5)
C6—O11—Ga1	127.6 (3)	C10—C9—H9A	109.3
C6—O12—Na1^{x}	120.1 (3)	C10—C9—H9B	109.3
O1—C1—H1	117.9	C9—C10—H10A	109.5
O2—C1—O1	124.2 (6)	C9—C10—H10B	109.5
O2—C1—H1	117.9	C9—C10—H10C	109.5
O3—C2—H2	117.4	H10A—C10—H10B	109.5
O4—C2—O3	125.1 (4)	H10A—C10—H10C	109.5
O4—C2—H2	117.4	H10B—C10—H10C	109.5
Ga1—O1—C1—O2	169.6 (4)	Na1^{vi}—O2—C1—O1	177.7 (4)
Ga1—O3—C2—O4	−179.2 (3)	Na1^{vii}—O4—C2—O3	−179.8 (3)
Ga1—O5—C3—O6	−178.8 (3)	Na1^{viii}—O6—C3—O5	179.5 (3)
Ga1—O7—C4—O8	179.2 (3)	Na1—O8—C4—O7	−165.7 (3)
Ga1—O9—C5—O10	178.9 (3)	Na1^{ix}—O10—C5—O9	172.5 (3)
Ga1—O11—C6—O12	177.5 (3)	Na1^{x}—O12—C6—O11	−170.9 (3)
391 K			
Ga1—O1	1.967 (10)	N1A—C7A	1.47 (8)
Ga1—O3	1.977 (5)	C7A—H7AA	0.9700
Ga1—O5	1.968 (9)	C7A—H7AB	0.9700
Ga1—O7	1.977 (5)	C7A—C8A	1.16 (5)
Ga1—O9	1.984 (5)	C8A—H8AA	0.9600
Ga1—O11	1.981 (6)	C8A—H8AB	0.9600
Na1—O2^{viii}	2.436 (15)	C8A—H8AC	0.9600
Na1—O4^{vii}	2.386 (11)	N2A—H2AA	0.8900
Na1—O6^{vi}	2.439 (15)	N2A—H2AB	0.8900
Na1—O8	2.435 (12)	N2A—H2AC	0.8900
Na1—O10^{x}	2.547 (8)	N2A—C9A	1.49 (3)
Na1—O12^{ix}	2.558 (8)	C9A—H9AA	0.9700
O1—C1	1.259 (18)	C9A—H9AB	0.9700
O2—Na1^{iii}	2.436 (15)	C9A—C10A	1.56 (2)
O2—C1	1.237 (19)	C10A—H10A	0.9600
O3—C2	1.291 (11)	C10A—H10B	0.9600
O4—Na1^{ii}	2.386 (11)	C10A—H10C	0.9600
O4—C2	1.200 (11)	N1B—H1BA	0.8900
O5—C3	1.270 (18)	N1B—H1BB	0.8900
O6—Na1^{i}	2.439 (15)	N1B—H1BC	0.8900
O6—C3	1.208 (19)	N1B—C7B	1.53 (6)
O7—C4	1.260 (10)	C7B—H7BA	0.9700

O8—C4	1.217 (11)	C7B—H7BB	0.9700
O9—C5	1.272 (11)	C7B—C8B	1.64 (3)
O10—Na1^{v}	2.547 (8)	C8B—H8BA	0.9600
O10—C5	1.222 (11)	C8B—H8BB	0.9600
O11—C6	1.263 (10)	C8B—H8BC	0.9600
O12—Na1^{iv}	2.558 (8)	N2B—H2BA	0.8900
O12—C6	1.226 (10)	N2B—H2BB	0.8900
C1—H1	0.9300	N2B—H2BC	0.8900
C2—H2	0.9300	N2B—C9B	1.37 (5)
C3—H3	0.9300	C9B—H9BA	0.9700
C4—H4	0.9300	C9B—H9BB	0.9700
C5—H5	0.9300	C9B—C10B	1.38 (4)
C6—H6	0.9300	C10B—H10D	0.9600
N1A—H1AA	0.8900	C10B—H10E	0.9600
N1A—H1AB	0.8900	C10B—H10F	0.9600
N1A—H1AC	0.8900		
O1—Ga1—O3	90.3 (3)	N1A—C7A—H7AA	103.2
O1—Ga1—O5	178.5 (5)	N1A—C7A—H7AB	103.2
O1—Ga1—O7	89.4 (3)	H7AA—C7A—H7AB	105.2
O1—Ga1—O9	89.0 (3)	C8A—C7A—N1A	136 (5)
O1—Ga1—O11	91.3 (3)	C8A—C7A—H7AA	103.2
O3—Ga1—O9	88.8 (2)	C8A—C7A—H7AB	103.2
O3—Ga1—O11	91.8 (2)	C7A—C8A—H8AA	109.5
O5—Ga1—O3	88.4 (3)	C7A—C8A—H8AB	109.5
O5—Ga1—O7	91.9 (3)	C7A—C8A—H8AC	109.5
O5—Ga1—O9	90.3 (3)	H8AA—C8A—H8AB	109.5
O5—Ga1—O11	89.4 (3)	H8AA—C8A—H8AC	109.5
O7—Ga1—O3	179.2 (3)	H8AB—C8A—H8AC	109.5
O7—Ga1—O9	90.5 (2)	H2AA—N2A—H2AB	109.5
O7—Ga1—O11	89.0 (3)	H2AA—N2A—H2AC	109.5
O11—Ga1—O9	179.3 (3)	H2AB—N2A—H2AC	109.5
O2^{viii}—Na1—O6^{vi}	175.6 (4)	C9A—N2A—H2AA	109.5
O2^{viii}—Na1—O10^{x}	85.6 (4)	C9A—N2A—H2AB	109.5
O2^{viii}—Na1—O12^{ix}	94.8 (4)	C9A—N2A—H2AC	109.5
O4^{vii}—Na1—O2^{viii}	91.5 (4)	N2A—C9A—H9AA	110.2
O4^{vii}—Na1—O6^{vi}	91.2 (5)	N2A—C9A—H9AB	110.2
O4^{vii}—Na1—O8	176.2 (5)	N2A—C9A—C10A	107.4 (15)
O4^{vii}—Na1—O10^{x}	95.8 (4)	H9AA—C9A—H9AB	108.5
O4^{vii}—Na1—O12^{ix}	84.4 (2)	C10A—C9A—H9AA	110.2
O6^{vi}—Na1—O10^{x}	90.6 (3)	C10A—C9A—H9AB	110.2
O6^{vi}—Na1—O12^{ix}	89.0 (4)	C9A—C10A—H10A	109.5
O8—Na1—O2^{viii}	87.0 (5)	C9A—C10A—H10B	109.5
O8—Na1—O6^{vi}	90.6 (4)	C9A—C10A—H10C	109.5
O8—Na1—O10^{x}	87.6 (2)	H10A—C10A—H10B	109.5
O8—Na1—O12^{ix}	92.3 (4)	H10A—C10A—H10C	109.5
O10^{x}—Na1—O12^{ix}	179.6 (6)	H10B—C10A—H10C	109.5
C1—O1—Ga1	126.3 (10)	H1BA—N1B—H1BB	109.5
C1—O2—Na1^{iii}	118.9 (9)	H1BA—N1B—H1BC	109.5
C2—O3—Ga1	126.2 (5)	H1BB—N1B—H1BC	109.5
C2—O4—Na1^{ii}	130.4 (7)	C7B—N1B—H1BA	109.5
C3—O5—Ga1	127.4 (9)	C7B—N1B—H1BB	109.5
C3—O6—Na1^{i}	119.3 (9)	C7B—N1B—H1BC	109.5
C4—O7—Ga1	127.8 (6)	N1B—C7B—H7BA	111.4
C4—O8—Na1	125.9 (6)	N1B—C7B—H7BB	111.4

C5—O9—Ga1	128.5 (6)	N1B—C7B—C8B	102 (2)
C5—O10—Na1^{v}	120.1 (6)	H7BA—C7B—H7BB	109.3
C6—O11—Ga1	127.7 (5)	C8B—C7B—H7BA	111.4
C6—O12—Na1^{iv}	119.9 (6)	C8B—C7B—H7BB	111.4
O1—C1—H1	117.8	C7B—C8B—H8BA	109.5
O2—C1—O1	124.4 (14)	C7B—C8B—H8BB	109.5
O2—C1—H1	117.8	C7B—C8B—H8BC	109.5
O3—C2—H2	117.4	H8BA—C8B—H8BB	109.5
O4—C2—O3	125.2 (9)	H8BA—C8B—H8BC	109.5
O4—C2—H2	117.4	H8BB—C8B—H8BC	109.5
O5—C3—H3	117.5	H2BA—N2B—H2BB	109.5
O6—C3—O5	125.1 (13)	H2BA—N2B—H2BC	109.5
O6—C3—H3	117.5	H2BB—N2B—H2BC	109.5
O7—C4—H4	117.4	C9B—N2B—H2BA	109.5
O8—C4—O7	125.1 (8)	C9B—N2B—H2BB	109.5
O8—C4—H4	117.4	C9B—N2B—H2BC	109.5
O9—C5—H5	116.9	N2B—C9B—H9BA	108.1
O10—C5—O9	126.2 (9)	N2B—C9B—H9BB	108.1
O10—C5—H5	116.9	N2B—C9B—C10B	117 (3)
O11—C6—H6	117.1	H9BA—C9B—H9BB	107.3
O12—C6—O11	125.9 (8)	C10B—C9B—H9BA	108.1
O12—C6—H6	117.1	C10B—C9B—H9BB	108.1
H1AA—N1A—H1AB	109.5	C9B—C10B—H10D	109.5
H1AA—N1A—H1AC	109.5	C9B—C10B—H10E	109.5
H1AB—N1A—H1AC	109.5	C9B—C10B—H10F	109.5
C7A—N1A—H1AA	109.5	H10D—C10B—H10E	109.5
C7A—N1A—H1AB	109.5	H10D—C10B—H10F	109.5
C7A—N1A—H1AC	109.5	H10E—C10B—H10F	109.5
Ga1—O1—C1—O2	172.5 (8)	Na1^{iii}—O2—C1—O1	178.2 (7)
Ga1—O3—C2—O4	179.2 (7)	Na1^{ii}—O4—C2—O3	−171.2 (7)
Ga1—O5—C3—O6	−176.6 (8)	Na1^{i}—O6—C3—O5	−179.5 (7)
Ga1—O7—C4—O8	−176.6 (7)	Na1—O8—C4—O7	178.1 (7)
Ga1—O9—C5—O10	−179.5 (6)	Na1^{v}—O10—C5—O9	173.3 (7)
Ga1—O11—C6—O12	178.1 (7)	Na1^{iv}—O12—C6—O11	−175.0 (8)

Symmetry code(s): (i) *x*−1/2, −*y*+1, *z*−1/2; (ii) *x*−1, *y*+1, *z*; (iii) *x*−1/2, −*y*+1, *z*+1/2; (iv) *x*, *y*+1, *z*; (v) *x*−1, *y*, *z*; (vi) *x*+1/2, −*y*+1, *z*+1/2; (vii) *x*+1, *y*−1, *z*; (viii) *x*+1/2, −*y*+1, *z*−1/2; (ix) *x*, *y*−1, *z*; (x) *x*+1, *y*, *z*.

Tab. S4. Selected hydrogen-bond parameters for (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$, at 293 and 391 K.

D*—H···*A	***D*—H (Å)**	**H···*A* (Å)**	***D*···*A* (Å)**	***D*—H···*A* (°)**
293 K				
C2—H2···O5	0.93	2.55	3.041 (5)	113.0
C4—H4···O1	0.93	2.49	2.953 (6)	110.7
N1—H1A···O7^{i}	0.89	2.09	2.974 (4)	176.0
N1—H1A···O8^{i}	0.89	2.55	3.158 (5)	125.9
N1—H1B···O12^{ii}	0.89	1.98	2.865 (5)	170.6
N1—H1C···O2	0.89	2.01	2.869 (5)	162.5
C7—H7A···O8^{i}	0.97	2.53	3.056 (6)	113.8
N2—H2A···O10	0.89	1.99	2.865 (4)	167.7
N2—H2B···O3^{iii}	0.89	2.13	2.971 (4)	156.4
N2—H2B···O4^{iii}	0.89	2.45	3.209 (5)	144.0
N2—H2C···O5^{ii}	0.89	2.58	3.277 (5)	135.7
N2—H2C···O6^{ii}	0.89	2.13	2.967 (5)	155.7
C9—H9B···O9	0.97	2.52	3.189 (6)	126.4
391 K				
C2—H2···O1	0.93	2.49	2.970 (13)	112.2
C4—H4···O5	0.93	2.57	3.031 (12)	111.4
N1A—H1AA···O12^{ii}	0.89	2.07	2.88 (9)	150.4
N1A—H1AB···O2	0.89	1.97	2.85 (8)	166.7
N1A—H1AC···O3^{iv}	0.89	2.18	3.02 (8)	157.7
N1A—H1AC···O4^{iv}	0.89	2.48	3.25 (7)	145.1
C7A—H7AB···O11^{ii}	0.97	2.41	3.15 (4)	132.9
N2A—H2AA···O7^{v}	0.89	2.29	3.11 (2)	152.8
N2A—H2AA···O8^{v}	0.89	2.52	3.31 (2)	148.3
N2A—H2AB···O5^{ii}	0.89	2.57	3.28 (3)	137.3
N2A—H2AB···O6^{ii}	0.89	2.20	3.00 (3)	149.7
N2A—H2AC···O10	0.89	1.86	2.74 (2)	168.1
C9A—H9AA···O9	0.97	2.39	3.127 (16)	132.5
C10A—H10A···O11^{vi}	0.96	2.64	3.442 (18)	141.1
N1B—H1BA···O12^{ii}	0.89	2.00	2.88 (6)	169.8
N1B—H1BB···O2	0.89	2.13	2.95 (5)	152.0
N1B—H1BC···O3^{iv}	0.89	2.05	2.93 (5)	173.9
N1B—H1BC···O4^{iv}	0.89	2.57	3.12 (4)	120.6
C7B—H7BA···O4^{iv}	0.97	2.42	2.98 (2)	116.3
C8B—H8BB···O1	0.96	2.55	3.40 (2)	148.2
C8B—H8BC···O11^{ii}	0.96	2.64	3.444 (19)	141.3
N2B—H2BA···O7^{v}	0.89	1.98	2.85 (4)	167.6
N2B—H2BA···O8^{v}	0.89	2.40	3.01 (4)	126.1
N2B—H2BB···O10	0.89	2.26	3.09 (4)	154.0
N2B—H2BC···O6^{ii}	0.89	2.04	2.91 (5)	165.0

Symmetry code(s): (i) *x*−1/2, −*y*+1, *z*+1/2; (ii) *x*−1, *y*, *z*; (iii) *x*−1/2, −*y*, *z*−1/2; (iv) *x*−1/2, −*y*+2, *z*+1/2; (v) *x*−1/2, −*y*+1, *z*−1/2; (vi) *x*−1/2, −*y*+2, *z*−1/2.

Tab. S5. Proposed assignment of Raman bands for (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$ and (**2**), $[CH_3CH_2NH_3]_2NaGa_{0.069}Cr_{0.931}(HCOO)_6$.

(1) (cm^{-1})	**(2)** (cm^{-1})	Assignment
3102_{vw}	3102_{vw}	$\nu(NH_3^+)$
3036_m, 3018_w, 2996_w, 2979_s, 2952_s, 2927_m	3035_m, 3017_w, 2995_w, 2978_s, 2952_s, 2927_m	$\nu(CH_3)+\nu(CH_2)$
2898_{vs}, 2885_{vs}, 2861_{vs}	2893_{vs}, 2880_{vs}, 2857_{vs}	$\nu(CH)$
2784_{vw}, 2753_w, 2120_{vw}	2785_{vw}, 2746_w, 2111_{vw}	ov+cb
1676_w, 1649_{vw}, 1628_{vw}	1671_w, 1648_{vw}, 1627_{vw}	$\delta_{as}(NH_3^+)+\nu_{as}(OCO)$
1588_{vw}	1589_{vw}	$\nu_{as}(OCO)$
1502_{vw}	1497_{vw}	$\delta_s(NH_3^+)$
1459_w, 1451_w	1458_w, 1451_w	$\delta(CH_3)+\delta(CH_2)$
1385_m, 1370_{sh}, 1340_m	1382_m, 1372_{sh}, 1338_m	$\delta_{ip}(CH)$
1326_w, 1320_{sh}, 1304_w	1328_w, 1318_{sh}, 1307_w	$\nu_s(OCO)$
1288_w, 1274_{vw}	1288_w, 1277_{vw}	$\rho(CH_2)+\nu_s(OCO)$
1229_{vw}, 1211_w	1230_{vw}, 1210_w	$\rho(CH_2)$
1058_w, 1049_w	1056_w, 1050_w	$\delta_{ip}(CH)+\nu_{as}(CCN)$
1012_{vw}, 999_{vw}	1011_{vw}, 997_{vw}	$\rho(NH_3^+)$
878_{sh}, 875_w	878_{sh}, 875_w	$\nu_s(CCN)$
804_w, 790_w	804_w, 790_w	$\delta(OCO)$
427_w	428_w	$\delta(CCN)$
338_w	341_w	$T'(Na^+)$
294_w, 255_w	243_w	$T'(Na^+)+T'(M^{III})+T'(HCOO^-)$
189_m, 163_m, 146_{sh}, 126_m, 109_{sh}	187_m, 163_m, 146_{sh}, 128_m, 108_{sh}	$L(HCOO^-)$

Key: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; ν, stretching vibration (s, symmetric; as, antisymmetric); δ, bending vibration (ip, in-plane; op, out-of-plane); ρ, rocking vibration; T', translation; L, libration.

Ta. S6. Proposed assignment of IR bands for (**1**), $[CH_3CH_2NH_3]_2NaGa(HCOO)_6$, at 80 and 400 K.

(1) (cm^{-1}) 80 K	**(1)** (cm^{-1}) 400 K	Assignment
3163_{vw}, $3074_{w,}$ 3052_w,	$3068_{vw,b}$	$\nu(NH_3^+)$
3026_{vw}, 3019_{vw}, 3012_{vw}, 2993_w, 2972_{vw}, 2948_{vw}, 2924_{vw}, 2905_{vw}	3030_{vw}, 2997_{vw}, 2978_s, 2984_{vw}, 2951_{vw}	$\nu(CH_3)+\nu(CH_2)$
2898_w, 2887_w, $2861_{vw,}$ 2841_{vw}, 2824_w	2880_{vw}, $2816_{vw,b}$	$\nu(CH)$
2757_{vw}, 2741_{vw}, 2723_{vw}, 2710_{vw}, 2666_{vw}, 2647_{vw}, 2636_{vw}, 2525_{vw}, 2516_{vw}	2753_{vw}, 2706_{vw}, 2655_{vw}, 2498_{vw}	ov+cb
1661_{sh}, 1655_{vs}, 1642_{vs}, 1634_{vs}, 1606_{vs}, 1603_{vs}	1644_{sh}, 1631_{vs}, 1611_{sh}	$\delta_{as}(NH_3^+)+\nu_{as}(OCO)$
1576_w	1589_{vw}	$\nu_{as}(OCO)$
1515_{vw}, 1505_{vw}	1500_{vw}	$\delta_s(NH_3^+)$
1472_{vw}, 1468_{vw}, 1461_{vw}, 1446_{vw}	1471_{vw}	$\delta(CH_3)+\delta(CH_2)$
1395_{vw}, 1387_w, 1377_{vw}, 1350_{vw}, 1340_w	1398_{sh}, 1386_w, 1344_{sh}	$\delta_{ip}(CH)$
1327_{vs}, 1324_{sh}, 1305_w	1325_s	$\nu_s(OCO)$
1284_s, 1273_{vw}	1297_{sh}, 1282_w	$\rho(CH_2)+\nu_s(OCO)$
1233_{vw}, 1213_{vw}, 1186_{vw}	1227_{vw}, 1207_{vw}	$\rho(CH_2)$
1053_{vw}	1048_{vw}, 1050_w	$\delta_{ip}(CH)+\nu_{as}(CCN)$

1019_{vw}, 1002_{vw}	1007_{vw}	$\rho(NH_3^+)$
816_{w}, 812_{sh}, 807_{w}, 791_{vw}, 787_{vw}	810_{w}, 806_{sh}, 793_{vw}	δ(OCO)

Key: s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; b, broad; ν, stretching vibration (s, symmetric; as, antisymmetric); δ, bending vibration (ip, in-plane; op, out-of-plane); ρ, rocking vibration; T', translation; L, libration.