Supporting information for

Theoretical prediction and experimental verification of the chemically-ordered atomic-laminate *i*-MAX phases $(Cr_{2/3}Sc_{1/3})_2GaC$ and $(Mn_{2/3}Sc_{1/3})_2GaC$

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Table SI. Prototype structure, with corresponding structural information, and calculated total energy per formula unit for considered competing phases within present paper.

Phase	Prototype	Pearson symbol	Space group	Energy (eV/fu)
Cr	W	cI2	Im-3m (229)	-9.6430
Cr	Cu	cF4	Fm-3m (225)	-9.2408
Cr	Mg	hP2	$P6_3/mmc$ (194)	-9.2298
Mn	α-Mn	cI58	I-43m (217)	-9.1582
Mn	β-Mn	cP20	$P4_132$ (213)	-9.1056
Mn	AuCu	tP4	P4/mmm (123)	-9.1297
Mn	CsCl	cP2	Pm-3m (221)	-9.0107
Sc	Mg	hP2	$P6_3/mmc$ (194)	-6.3327
Sc	Np	tP4	P4/nmm (129)	-6.2230
Sc	Sc	hP6	P6122 (178)	-6.2006
α-Ga	Ga	oC8	Cmca (64)	-3.0302
Ga	Ga	oC4	Cmcm (63)	-3.0121
Ga	Ga	mC4	C2/c (15)	-3.0119
C	C (graphite)	hP4	$P6_3/mmc$ (194)	-9.2246
$Cr_{23}C_6$	$Cr_{23}C_6$	cF116	Fm-3m (225)	-279.3407

Cr_3C	Fe_3C	oP16	Pnma (62)	-38.4634
Cr_7C_3	Cr_7C_3	oP40	Pnma (62)	-96.2272
Cr_3C_2	Sb_2S_3	oP20	Pnma (62)	-47.9107
$Mn_{23}C_6$	$Cr_{23}C_6$	cF116	Fm-3m (225)	-268.6277
Mn_3C	Fe_3C	oP16	C2/c (15)	-64.7226
Mn_5C_2	Mn_5C_2	mS28	Pnma (62)	-92.4925
Mn_7C_3	Cr_7C_3	oP40	P63mc (186)	-92.4221
MnC	NiAs	hP4	$P6_3/mmc$ (194)	-18.1687
Sc_2C	CdI_2	hP3	P3m1 (156)	-23.2708
Sc_2C	Ti_2C	cF48	Fd-3m (227)	-23.2657
Sc_4C_3	Th_3P_4	cI28	I-43d (220)	-56.4192
$ScC_{0.875}$	NaCl	cF8	Fm-3m (225)	-14.9227
ScC	NaCl	cF8	Fm-3m (225)	-15.8395
Sc_3C_4	Sc_3C_4	tP70	P4/mnc (128)	-58.7638
Cr_3Ga	Cr_3Si (β-W)	cP8	Pm-3n (223)	-32.1352
CrGa	MnGa	hR78	R-3m (166)	-12.7091
Cr_3Ga_4	Fe_3Ga_4	mS42	C12/m1 (12)	-41.2187
$CrGa_4$	Hg_4Pt	cI10	Im-3m (229)	-22.5270
Mn_3Ga	$TiAl_3$	tI8	I4/mmm (139)	-30.9155
Mn_3Ga	Ni_3Sn	hP8	$P6_3/mmc$ (194)	-30.6467
MnGa	AuCu	tP2	P4/mmm (123)	-12.4531
MnGa	CuPt	hR32	R-3m (166)	-12.1692
MnGa	Mg	hP2	$P6_3/mmc$ (194)	-12.2589
MnGa	MnGa	hR78	R-3m (166)	-12.4090
Mn_5Ga_8	Cr_5Al_8	hR26	R3m (160)	-70.6863
Mn_2Ga_5	Mn_2Hg_5	tP14	P4/mbm (127)	-34.3720
$MnGa_4$	$PtHg_4$	cI10	Im-3m (229)	-22.1774
$MnGa_6$	$MnAl_6$	oC28	Cmcm (63)	-27.5430
Sc_5Ga_3	Y_5Ga_3	mS32	C12/m1 (12)	-44.9893
$Sc_{11}Ga_{10}$	$Ho_{11}Ge_{10}$	tI84	I4/mmm (139)	-112.2262
ScGa	TlI	oS8	Cmcm (63)	-9.0837
$ScGa_2$	KHg_2	oI12	Imma (74)	-14.0796
$ScGa_3$	$AuCu_3$	cP4	Pm-3m (221)	-17.3922
Cr_3GaC	$CaTiO_3$	cP5	Pm-3m (221)	-41.0458
Cr_3GaC	Re_3B	oP20	Cmcm (63)	-41.4353
Cr_2GaC	Cr_2AlC	hP8	$P6_3/mmc$ (194)	-32.0973
Cr_3GaC_2	Ti_3SiC_2	hP12	$P6_3/mmc$ (194)	-50.6991
Cr_4GaC_3	Ti_4AlN_3	hP12	$P6_3/mmc$ (194)	-69.3788
Mn_3GaC	$CaTiO_3$	cP5	Pm-3m (221)	-40.2921
Mn_3GaC	Re_3B	oP20	Cmcm (63)	-40.3287
Mn_3GaC	Cr_3AsN	tI20	I4/mcm (140)	-40.2893
Mn_2GaC	Cr_2AlC	hP8	$P6_3/mmc$ (194)	-31.1598
Mn_3GaC_2	Ti_3SiC_2	hP12	$P6_3/mmc$ (194)	-49.2157
Mn_4GaC_3	Ti_4AlN_3	hP12	$P6_3/mmc$ (194)	-67.0531
Sc_3GaC	$CaTiO_3$	cP5	Pm-3m (221)	-34.2348
Sc_2GaC	Cr_2AlC	hP8	P63/mmc (194)	-27.0471
Sc_3GaC_2	Ti_3SiC_2	hP12	P63/mmc (194)	-43.0551
Sc_4GaC_3	Ti_4AlN_3	hP16	P63/mmc (194)	-58.9402
Sc_2CrC_3	Sc_2CrC_3	oP24	Pbam (55)	-52.4688
β-$ScCrC_2$	$ScCrC_2$	hP8	$P6_3/mmc$ (194)	-35.8144
Cr_2ScGaC_2	Cr_2TiAlC_2	hP12	$P6_3/mmc$ (194)	-48.4666
Sc_2CrGaC_2	Cr_2TiAlC_2	hP12	$P6_3/mmc$ (194)	-45.8395
$CrSc_2C$	$CuHg_2Ti$	cF16	F-43m (216)	-27.7394

$CrSc_2C$	$AlCu_2Mn$	cF16	Fm-3m (225)	-28.4508
$ScMn_2$	$MgZn_2$	hP12	$P6_3/mmc$ (194)	-25.0744
$MnSc_2C$	$CuHg_2Ti$	cF16	F-43m (216)	-28.1878
$MnSc_2C$	$AlCu_2Mn$	cF16	Fm-3m (225)	-28.9198
$Sc_3Mn_2Ga_6$	$Sc_3Mn_2Ga_6$	oP44	Pnma (62)	-60.5657

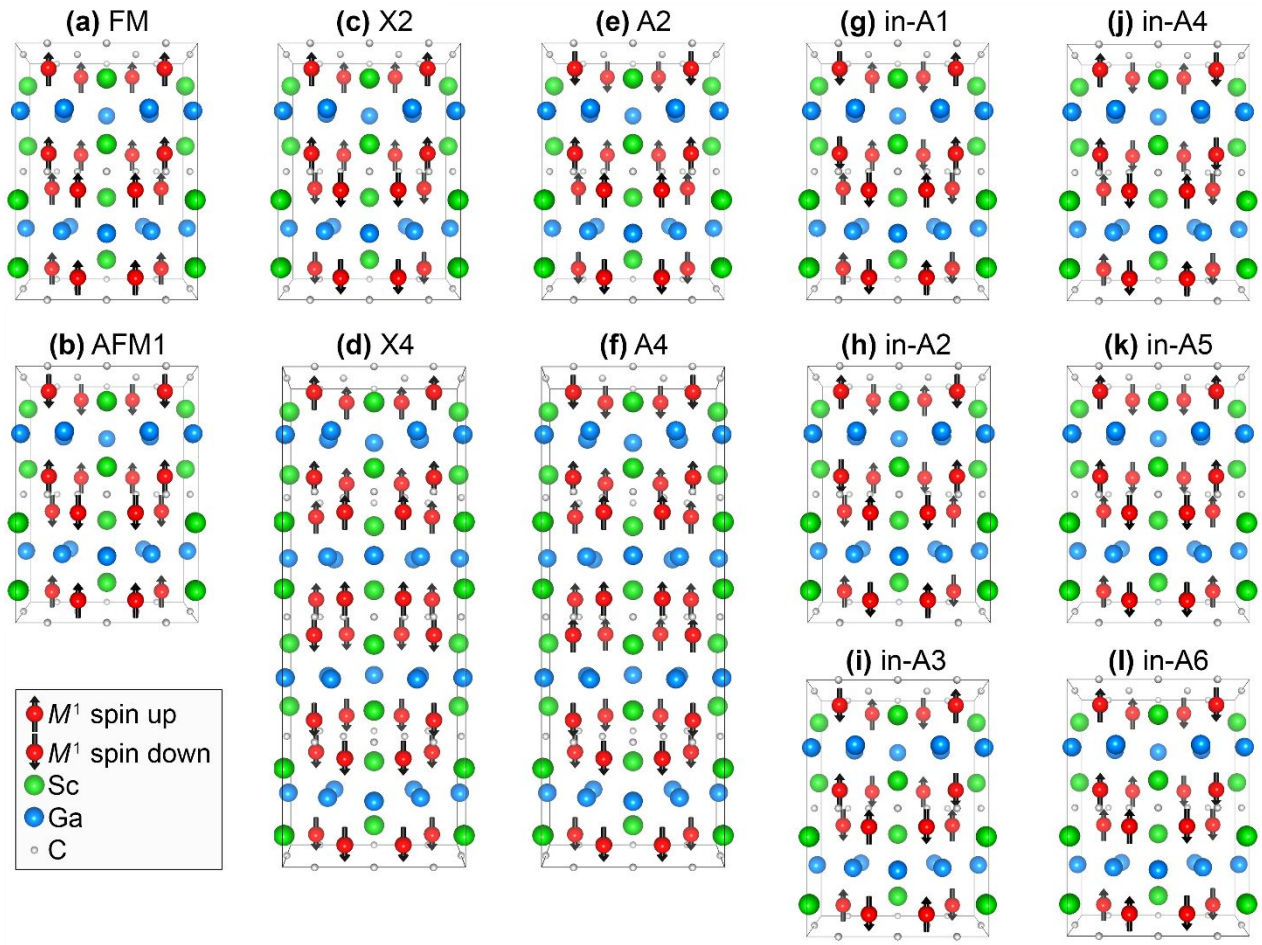

Figure S1. Schematic representation of 12 collinear spin configurations considered for $\left(M^1_{2/3}Sc_{1/3}\right)_2GaC$, M^1 = Cr or Mn, where the spin direction at each M^1 site is represented by a black arrow.

Table SII. Identified equilibrium simplex and corresponding formation enthalpy for Cr_2GaC, Mn_2GaC and Sc_2GaC phases ($P6_3/mmc$ structure), and the hypothetical *i*-MAX phases $(Sc_{2/3}Cr_{1/3})_2GaC$ and $(Sc_{2/3}Mn_{1/3})_2GaC$. Please note that the former *i*-MAX phase diverge from an *i*-MAX structure upon relaxation, i.e. the phase is not stable for such atom configuration. Relaxation performed using the PBE exchange-correlation functional.

Phase	equilibrium simplex	Spin configuration†	ΔH_{cp} (meV/atom)	experimental observation
Cr_2GaC	Cr_3C_2, $CrGa_4$, Cr_7C_3	in-AFM1	-19	yes
Mn_2GaC	Mn_3GaC, C, $MnGa_4$	$AFM[0001]_4^A$	-31	yes
Sc_2GaC	Sc_3GaC, $ScGa_2$, Sc_3C_4	NM	11	no
$(Sc_{2/3}Cr_{1/3})_2GaC$	$(Cr_{2/3}Sc_{1/3})_2GaC$, $ScGa_2$, Sc_3GaC, Sc_2CrC_3	NM	-5	no
$(Sc_{2/3}Mn_{1/3})_2GaC$	$(Mn_{2/3}Sc_{1/3})_2GaC$, Sc_3GaC, $ScGa_2$, Sc_3C_4	NM	+12	no

† Results attained form Ref. [10] for Cr_2GaC and Ref. [11] for Mn_2GaC.

Table SIII. Calculated energy and corresponding structural and magnetic information for $(Cr_{2/3}Sc_{1/3})_2GaC$ when considering different spin configurations. Relaxation performed using the PBE exchange-correlation functional.

Spin configuration	Space group	a (Å)	b (Å)	c (Å)	Notes	ΔE_{NM} (meV/atom)	magnetic moment (μ_B / Cr atom)
NM	63	9.0569	5.1800	12.7669		0	0.00
FM	63	9.0926	5.2088	12.7481		-0.7	0.73
AFM1			goes to the NM state				
X2	63	9.0708	5.1951	12.7722		-1.7	0.72
A2			goes to the NM state				
X4	12	5.2075	9.0888	12.7550	β=90.0872°	-1.0	0.79, 0.80
A4	38	12.7541	9.0600	5.1864	mix of A2 and AFM1	-0.7	0.48, 0.61
in-AFM1			goes to the NM state				
in-AFM2			goes to the NM state				
in-AFM3			goes to the NM state				
in-AFM4			goes to the NM state				
in-AFM5			goes to the NM state				
in-AFM6	63	9.0791	5.1957	12.7547		-2.7	0.63

Table SIV. Calculated energy and corresponding structural and magnetic information for $(Mn_{2/3}Sc_{1/3})_2GaC$ when considering different spin configurations. Relaxation performed using the PBE exchange-correlation functional.

Spin configuration	Space group	a (Å)	b (Å)	c (Å)	Notes	ΔE_{NM} (meV/atom)	magnetic moment (μ_B / Mn atom)
NM	63	8.9901	5.1385	12.5482		0	0.00
FM			goes to the NM state				
AFM1	63	8.9900	5.1419	12.5850		-1.1	0.72
X2			goes to the NM state				
A2			goes to the NM state				
X4	12	5.1397	8.9914	12.5611	β=90.0032° mix of A2 and AFM1	-0.2	0.24, 0.50
A4			goes to the NM state				
in-AFM1			goes to the NM state				
in-AFM2			goes to the NM state				
in-AFM3			goes to the NM state				
in-AFM4			goes to the NM state				
in-AFM5			goes to the NM state				
in-AFM6			goes to the NM state				

Table SV. Calculated energy and corresponding structural and magnetic information for $(Cr_{2/3}Sc_{1/3})_2GaC$ when considering different spin configurations. Relaxation performed using the PBE exchange-correlation functional with +U method, where U_{eff} = 1 eV.

Spin configuration	Space group	a (Å)	b (Å)	c (Å)	Notes	ΔE_{NM} (meV/atom)	magnetic moment (μB / Cr atom)
NM	63	9.0533	5.1824	12.7838		0	0.00
FM	63	9.0995	5.2364	12.8101		-24	1.29
AFM1	63	9.1256	5.2570	12.8569		-23	1.57
X2	63	9.1169	5.2460	12.8462		-31	1.56
A2	63	9.1105	5.2521	12.8189		-22	1.37
X4	12	5.2422	9.1015	12.8323	β=90.0220°	-28	1.30, 1.54
A4	38	12.8135	9.1030	5.2444		-24	1.29, 1.36
in-AFM1	63	9.0833	5.1917	12.7655		-1.5	0.55
in-AFM2	63	9.0572	5.1995	12.7896		-0.6	0.54
in-AFM3			goes to the NM state				
in-AFM4	63	9.0748	5.2260	12.7770		-5.7	1.00
in-AFM5	63	9.0598	5.2282	12.8228		-29	1.06
in-AFM6	63	9.1202	5.2123	12.7778		-29	1.06

Table SVI. Calculated energy and corresponding structural and magnetic information for $(Mn_{2/3}Sc_{1/3})_2GaC$ when considering different spin configurations. Relaxation performed using the PBE exchange-correlation functional with +U method, where U_{eff} = 1 eV.

Spin configuration	Space group	a (Å)	b (Å)	c (Å)	Notes	ΔE_{NM} (meV/atom)	magnetic moment (μ_B / Mn atom)
NM	63	8.9848	5.1348	12.5553		0	0.00
FM	63	9.1086	5.2834	12.7238		-25	2.16
AFM1	63	9.0510	5.1932	12.7282		-39	1.90
X2	63	9.0618	5.2280	12.7330		-31	2.07
A2	63	9.1072	5.2792	12.6762		-26	2.31
X4	12	5.2438	9.0707	12.6985	90.2385	-28	2.05, 2.21
A4	38	12.6983	9.1109	5.2807		-26	2.34, 2.40
in-AFM1	63	9.0407	5.1684	12.6277		-4.2	1.27
in-AFM2	63	8.9809	5.2704	12.8601		-25	2.24
in-AFM3	63	9.1208	5.1892	12.7721		-22	2.10
in-AFM4	63	8.9605	5.2779	12.8983		-2.8	2.29
in-AFM5	63	9.0087	5.2494	12.7079		-15	1.92
in-AFM6	63	9.0231	5.2354	12.6943		-16	1.84

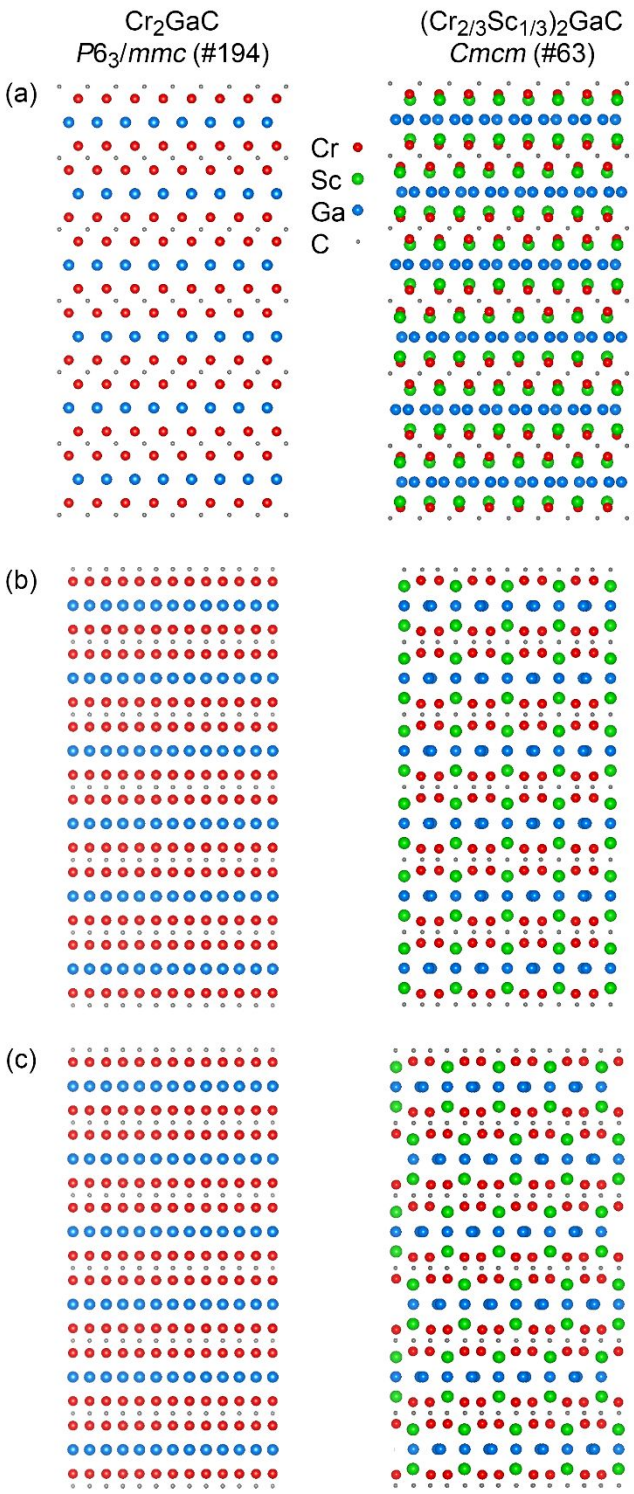

Figure S2. Schematic representation of the Cr_2GaC MAX phase and $(Cr_{2/3}Sc_{1/3})_2GaC$ *i*-MAX phase when viewed along a) [100], b) [010] and c) [110] zone axis. The primary structural difference between the MAX phase and the *i*-MAX phase is the in-plane chemical order within the *M*-layer,

to allow formation of a honeycomb pattern where the larger elements approach the A-layer. The A-layer, in turn, change its structure into Kagomé-like ordering, altogether resulting in an orthorhombic crystal structure of space group *Cmcm* for the herein reported phases. Based on previously reported theoretical analysis of structure, bonding, and related stability, we suggest that the formation of *i*-MAX is favored for increasing size difference between the two metals, and with decreasing size of the A-element.

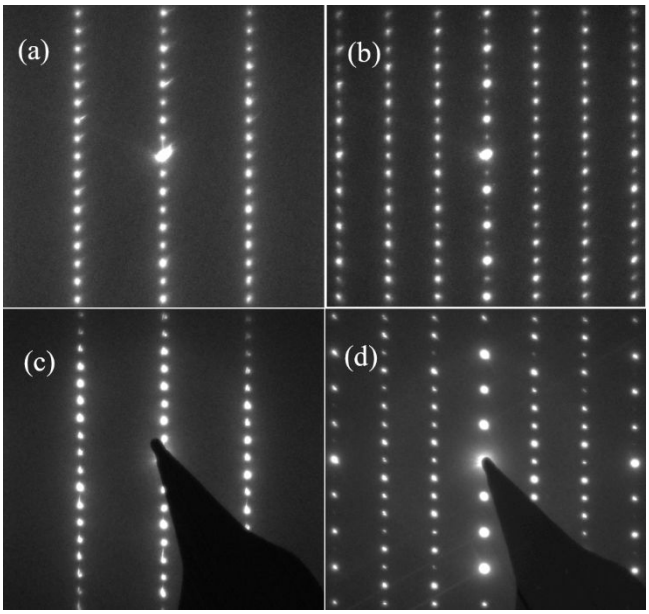

Figure S3. Selected area electron diffraction (SAED) of $(Cr_{2/3}Sc_{1/3})_2GaC$ along the [100] (a) and [110] (b) zone axis, and of $(Mn_{2/3}Sc_{1/3})_2GaC$ along the [100] (c) and [110] (d) zone axis.

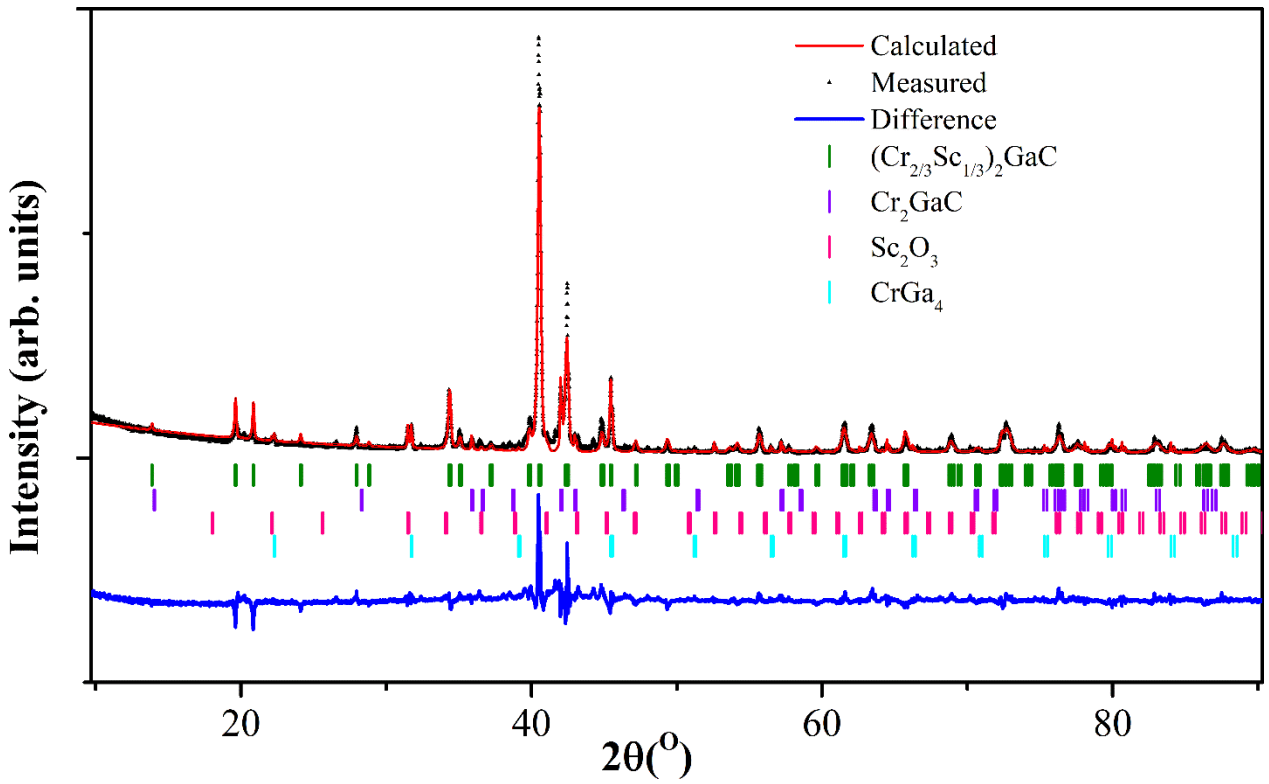

Figure S4. Rietveld refinement of XRD data for the $(Cr_{2/3}Sc_{1/3})_2GaC$ sample.

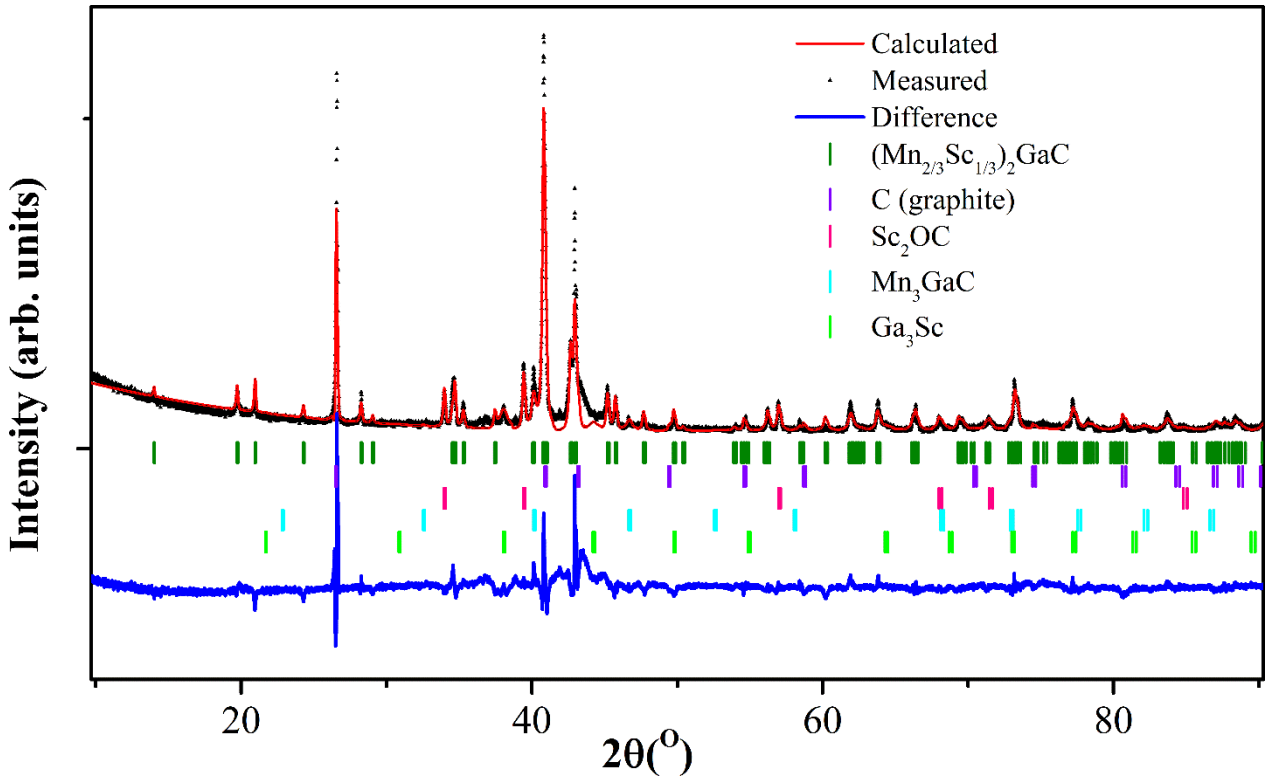

Figure S5. Rietveld refinement of XRD data for the $(Mn_{2/3}Sc_{1/3})_2GaC$ sample.

Table SVII. Cell parameters and atom coordinates obtained from XRD Rietveld refinement at RT. Upon attempted change in occupancy (from 1.0) as well as Cr/Mn intermixing, there was no improvement in the refinement.

Space group	*Cmcm* (#63)	*Cmcm* (#63)
System	Cr-Sc-Ga-C	Mn-Sc-Ga-C
χ^2	13.0	10.1
a (Å)	9.05649(34)	8.99827(60)
b (Å)	5.21497(20)	5.19006(36)
c (Å)	12.76932(40)	12.62758(46)
	$\alpha = \beta = \gamma = 90°$	
M^1	Cr, 16h	Mn, 16h
	0.8364(2)	0.8364(14)
	0.3269(17)	0.3251(30)
	0.5771(3)	0.5761(4)
Sc	8f	8f
	0.0000	0.0000
	0.1671(23)	0.1815(31)
	0.3914(5)	0.3910(5)
Ga	4c	4c
	0.0000	0.0000
	0.6799(16)	0.6762(18)
	0.2500	0.2500
	8g	8g
	0.7655(5)	0.76362(9)
	0.4071(11)	0.43975(13)
	0.2500	0.2500
C	8e	8e
	0.8410(30)	0.8590(32)
	0.0000	0.0000
	0.0000	0.0000
	4b	4b
	0.0000	0.0000
	0.5000	0.5000
	0.0000	0.0000

Table SVIII. Phase purity obtained from Rietveld refinement in wt.%

System	Composition				
Cr-Sc-Ga-C	$(Cr_{2/3}Sc_{1/3})_2GaC$ 86.8%	Cr_2GaC 6.1%	Sc_2O_3 4.1%		$CrGa_4$ 3.0%
Mn-Sc-Ga-C	$(Mn_{2/3}Sc_{1/3})_2GaC$ 61.4%	C (graphite) 25.1%	Sc_2OC 6.8%	Mn_3GaC 3.2%	Ga_3Sc 3.5%