Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Evidence of Cationic Mixing and Ordering in the Honeycomb Layer of Li_4MSbO_6 (M(III) = Cr, Mn, Al, Ga) (S.G. *C2/c*) Oxides

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Fig. S4. Structure of Li_4MSbO_6 (M = **(a)** Cr (SCXRD), **(b)** Cr (PXRD), **(c)** Mn, **(d)** Ga) perpendicular to the honeycomb layers.

Fig. S5. PXRD patterns of $Ag_3LiMSbO_6$ where M = **(a)** Cr, **(b)** Mn, **(c)** Fe, **(d)** Al, **(e)** Ga.

Fig. S6. Diffuse reflectance spectra of $Ag_3LiMSbO_6$ (M = **(a)** Cr, **(b)** Fe, **(c)** Mn, **(d)** Al, **(e)** Ga).

Table S1: Representative examples of oxides with rocksalt superstructures.

Stoichiometry	Compound (Isostructural analogues)	*a* (Å)	*b* (Å)	*c* (Å)	*β* (°)	*S.G.*	Ref.
ABO_2	γ - $LiFeO_2$	4.05		8.74		*$I4_1/amd$*	[1]
	($LiMO_2$; M = Sc, In						
	$NaMO_2$; M = Gd, Eu, Sm, Nd)						
	α – $NaFeO_2$	3.027(1)		16.12(2)		*R-3m*	[2]
	($LiMO_2$; M = Co, Mn, Ni, V, Cr)						
A_2MXO_4	Li_2ZrMgO_4	4.209(1)		9.145(2)		*$I4_1/amd$*	[3]
	(Li_2MXO_4; M = Zr, Hf; X = Mn, Fe, Co, Ni, Cu, Zn)						
A_2BO_3	Li_2TiO_3	5. 069(2)	8.799(7)	9. 7599(9)	100.1(1)	*C2/c*	[4]
	Li_2MnO_3	4.9246(1)	8.5216(1)	5.0245(1)	109.398(1)	*C2/m*	[5]
	Li_2RuO_3	5.0466(3)	8.7649(2)	5.9417(3)	124.495(3)	*C2/m*	[6]
A_3BO_4	Li_3RuO_4	5.1057(1)	5.8545(1)	5.1062(1)	110.039(1)	*P2/a*	[7]
	α – Na_3BiO_4	5.87(1)	6.69(6)	5.65 (0)	109.8	*P2/c*	[8]
A_5BO_6	Li_5ReO_6	5.062(5)	8.738(8)	5.032(4)	110.29(6)	*C2/m*	[9]
$A_3M_2XO_6$	$Li_3Ni_2SbO_6$	5.1828(2)	8.9677(3)	5.1577(2)	109.69(2)	*C2/m*	[10]
	$Li_3Cu_2SbO_6$	5.4659(1)	8.7272(2)	9.7807(3)	95.080(2)	*C2/c*	[11]
	$Li_3Zn_2SbO_6$	5.259(3)	9.036(7)	5.209(4)	110.49(3)	*C2/m*	[12]
	$Li_3Ni_2BiO_6$	5.2581(4)	9.116(1)	5.1969(8)	109.33(1)	*C2/m*	[13] [12]
	($Li_3Zn_2BiO_6$)						
	$Na_3Mg_2SbO_6$	5.3285(1)	9.1908(1)	5.6711(1)	108.30(1)	*C2/m*	[14] [15]
	($Na_3M_2SbO_6$; M = Co, Cu, Zn)						
$A_2M_2XO_6$	$Li_2Ni_2TeO_6$	5.8921(7)	8.599(1)	17.691(2)		*Fddd:2*	[16]
	$Li_2Cu_2TeO_6$	5.6435(7)	8.607(1)	5.3515(6)	115.222(2)	*C2/m*	[16]
	$Na_2Mg_2TeO_6$	5.253(1)		11.2603(2)		*$P6_322$*	[15] [17]
	($Na_2Co_2TeO_6$)						
	$Na_2Ni_2TeO_6$	5.2042(5)		11.1383(5)		*$P6_3/mcm$*	[17]
	$Na_2Cu_2TeO_6$	5.7059(6)	8.6751(9)	5.9380(6)	113.740(2)	*C2/m*	[18]
$A_3MM'XO_6$	$Li_3NiMgBiO_6$	5.2612(7)	9.097(1)	5.2212(6)	109.62(1)	*C2/m*	[13]
	($Li_3NiMBiO_6$; M = Cu, Zn)						

$A_3(LiMX)O_6$	$Na_3LiFeSbO_6$	5.3274(2)	9.2049(4)	11.377(3)	108.47(1)	*C2/c*	[19]
	Li_4FeSbO_6	5.1706(5)	8.9382(5)	5.1635(2)	109.49(1)	*C2/m*	[20]
	Li_4NiTeO_6	5.1603(3)	8.8914(5)	5.1426(4)	110.209(3)	*C2/m*	[21]
	(Li_4MTeO_6; M = Cu, Zn)						

Table S2: Comparison of the indexation*of the powder X-ray diffraction patterns in *C2/m* and *C2/c* space groups for Li_4CrSbO_6.

Li_4CrSbO_6										
C2/c						***C2/m***				
2θ (obs)	***h***	***k***	***l***	**2θ (cal)**	**Δ2θ**	***h***	***k***	***l***	**2θ (cal)**	**Δ2θ**
18.46	0	0	2	18.3942	0.0725	0	0	1	18.4260	0.0407
20.14	0	2	0	20.0933	0.0556	0	2	0	20.0241	0.1159
21.00	-1	1	1	20.9527	0.0508	1	1	0	20.9390	0.0645
22.15	0	2	1	22.1255	0.0284					
23.56	1	1	1	23.5323	0.0338	-1	1	1	23.5000	0.0661
25.33	-1	1	2	25.3007	0.0324					
27.37	0	2	2	27.3717	0.0024	0	2	1	27.3420	0.0321
29.54	1	1	2	29.5419	0.0002					
31.92	-1	1	3	31.9258	-0.0005	1	1	1	31.9697	-0.0444
34.46	0	2	3	34.4948	-0.0348					
35.65	-1	3	1	35.6940	-0.0440	-2	0	1	35.5349	0.1151
37.28	0	0	4	37.2849	-0.0049	-1	3	1	37.2353	0.0447
40.77	-2	2	1	40.8128	-0.0463	-2	2	1	41.1220	-0.3520
42.63	-2	2	2	42.6502	-0.0142	2	2	0	42.6212	0.0088
43.28	2	0	2	43.2639	0.0258	-2	0	2	43.2233	0.0664
47.36	-2	0	4	44.3767	-0.0099	-1	3	2	47.4121	-0.0453
54.73	-3	1	1	54.7128	0.0172	-3	1	1	54.6628	0.0672
57.22	2	0	4	57.2586	-0.0306	-2	0	3	57.2425	-0.0225
Lattice parameter	*a* = 5.126(3); *b* = 8.838(7); *c* = 9.796(8); *β* = 100.05(9)º					a = 5.129(35); *b*=8.868(28); c = 5.112(4); *β* = 109.6(7)º				

* Celref software was used for indexing the PXRD pattern

Table S3: Comparison of the indexation*of the powder X-ray diffraction patterns in *C2/m* and *C2/c* space groups for Li_4MnSbO_6.

Li_4MnSbO_6										
C2/c						*C2/m*				
2θ (obs)	***h***	***k***	***l***	**2θ (cal)**	**Δ2θ**	***h***	***k***	***l***	**2θ (cal)**	**Δ2θ**
18.30	0	0	2	18.2821	0.0179	0	0	1	18.3189	-0.0189
20.13	0	2	0	20.1196	0.0104	0	2	0	20.0973	0.0327
20.36	1	1	0	20.3661	-0.0061					
21.04	-1	1	1	21.0423	-0.0023	1	1	0	20.9204	0.1131
22.13	0	2	1	22.1261	0.0039					
23.62	1	1	1	23.5915	0.0285	-1	1	1	23.5259	0.0941
25.29	-1	1	2	25.3238	-0.0338					
27.31	0	2	2	27.3147	-0.0047	0	2	1	27.3231	-0.0131
29.55	1	1	2	29.5277	0.0223					
31.84	-1	1	3	31.8692	-0.0292	1	1	1	31.7973	0.0427
34.35	0	2	3	34.3705	-0.0205					
35.79	-1	3	1	35.7799	0.0101	1	3	0	35.6789	0.1111
37.07	0	0	4	37.0516	0.0184	0	0	2	37.1282	-0.0582
37.42	-2	0	2	37.4121	0.0079					
41.03	-2	2	1	41.0421	-0.0121	-2	2	1	41.1846	-0.1546
43.36	2	0	2	43.3885	-0.0285	-2	0	2	43.2468	0.1132
47.44	-2	0	4	47.4181	0.0219	-1	3	2	47.4256	0.0144
50.03	0	4	3	50.0340	-0.0040					
55.16	1	5	0	55.1558	0.0042	-2	4	1	55.2551	-0.0951
57.16	-1	3	5	57.1668	-0.0068	-2	0	3	57.1815	-0.0215
58.55	-3	1	3	58.5409	0.0091					
Lattice parameter	*a* = 5.091(2); *b* = 8.826(2); c = 9.853(4); *β* = 99.966(2)º					*a* = 5.129(30); *b*= 8.836(18); *c* = 5.130(24); *β* =109.2(5)º				

* Celref software was used for indexing the PXRD pattern

Table S4: Comparison of the powder X-ray diffraction patterns indexation* in *C2/m* and *C2/c* space groups for Li_4FeSbO_6.

Li_4FeSbO_6										
C2/c						***C2/m***				
2θ (obs)	***h***	***k***	***l***	**2θ (cal)**	**Δ2θ**	***h***	***k***	***l***	**2θ (cal)**	**Δ2θ**
18.17	0	0	2	18.1816	-0.0116	0	0	1	18.11	0.06
19.79	0	2	0	19.7241	0.0659	0	2	0	19.6954	0.0946
20.68	-1	1	1	20.6194	0.0606	1	1	0	20.6308	0.0492
23.23	1	1	1	23.2087	0.0213	-1	1	1	23.1483	0.0817
26.94	0	2	2	26.9502	-0.0102	0	2	1	26.8795	0.0605
31.5	-1	1	3	31.4659	0.0341	1	1	1	31.4415	0.0585
35.05	-1	3	1	35.0553	-0.0053	-2	0	1	35.0389	0.0111
36.64	-2	0	2	36.6369	0.0031	-1	3	1	36.6318	0.0082
40.11	0	4	0	40.065	0.045	0	4	0	40.0048	0.1052
40.52	2	2	0	40.5394	-0.0194	-2	2	1	40.5128	0.0072
41.96	-2	2	2	41.9471	0.0129	2	2	0	41.9712	-0.0112
42.64	-1	3	3	42.6414	-0.0014	1	3	1	42.5939	0.0461
44.28	0	4	2	44.3251	-0.0451	0	4	1	44.2376	0.0424
46.62	-2	0	4	46.6557	-0.0357	-1	3	2	46.6045	0.0155
53.9	1	3	4	53.8993	0.0007	-1	1	3	53.8784	0.0216
54.25	-1	5	1	54.2738	-0.0238	-2	4	1	54.2144	0.0356
55.44	1	5	1	55.4554	-0.0154	0	4	2	55.4004	0.0396
56.33	2	4	1	56.317	0.013	1	3	2	56.331	-0.001
61.78	-3	3	1	61.7888	-0.0088	-3	3	1	61.7857	-0.0057
64.93	-1	3	6	64.9193	0.0107	-3	3	2	64.9359	-0.0059
Lattice parameter	a = 5.198(4); b = 8.994(3); c = 9.907(9); β = 100.2(1)°					a = 5.197(7); b = 8.994(4); c = 5.192(7); β = 109.5(1)°				

* Celref software was used for indexing the PXRD pattern

Table S5: Comparison of the indexation*powder X-ray diffraction patterns in *C2/m* and *C2/c* space groups for Li_4AlSbO_6.

Li_4AlSbO_6										
C2/c						***C2/m***				
2θ (obs)	**h**	**k**	**l**	**2θ (cal)**	**Δ2θ**	**h**	**k**	**l**	**2θ (cal)**	**Δ2θ**
18.54	0	0	2	18.4965	0.0435	0	0	1	18.4567	0.0833
20.45	0	2	0	20.3743	0.0757	0	2	0	20.3737	0.0763
20.67	1	1	0	20.5747	0.0653					
21.32	-1	1	1	21.2875	0.0325	1	1	0	21.2902	0.0298
22.47	0	2	1	22.4033	0.0667					
23.92	1	1	1	23.8182	0.1018	-1	1	1	23.7958	0.1242
25.63	-1	1	2	25.6444	-0.0144					
27.64	0	2	2	27.6522	-0.0122	0	2	1	27.6245	0.0155
32.22	-1	1	3	32.2856	-0.0656	1	1	1	32.259	-0.039
34.91	0	2	3	34.7939	0.1161					
36.18	2	0	0	36.1552	0.0248	-2	0	1	36.1496	0.0304
37.4	1	1	3	37.3846	0.0154					
37.81	1	3	1	37.8418	-0.0318	-1	3	1	37.8264	-0.0164
41.44	0	4	0	41.4311	0.0089	0	4	0	41.4298	0.0102
41.87	2	2	0	41.8529	0.0171	-2	2	1	41.8477	-0.0077
43.77	2	0	2	43.7896	-0.0196	-2	0	2	43.7376	0.0324
45.76	0	4	2	45.7256	0.0344	0	4	1	45.7068	0.0532
47.86	1	3	3	47.9751	-0.1151	-1	3	2	47.9148	-0.0548
55.71	-3	1	1	55.698	0.012	-3	1	1	55.7035	0.0065
56.04	2	4	0	56.1394	-0.0994	-2	4	1	56.1344	-0.0944
57.64	0	0	6	57.6501	-0.0101	-2	0	3	57.6781	-0.0381
Lattice parameter	a = 5.038 (9); b = 8.7106(7); c = 9.727(1); β = 99.7(3)º					a = 5.037(1); b = 8.710(7); c = 5.094(2); β = 109.4(3)º				

* Celref software was used for indexing the PXRD pattern

Table S6: Comparison of the indexation* of the powder X-ray diffraction patterns in *C2/m* and *C2/c* space groups for Li_4GaSbO_6.

Li_4GaSbO_6										
C2/c						*C2/m*				
2θ (obs)	***h***	***k***	***l***	**2θ (cal)**	**Δ2θ**	***h***	***k***	***l***	**2θ (cal)**	**Δ2θ**
18.26	0	0	2	18.2727	-0.0127	0	0	1	18.2623	-0.0023
19.98	0	2	0	19.9988	-0.0188	0	2	0	19.9883	-0.0083
20.21	1	1	0	20.2219	-0.0119					
20.88	-1	1	1	20.9017	-0.0217	1	1	0	20.8915	-0.0115
22	0	2	1	22.0138	-0.0138					
23.45	1	1	1	23.4633	-0.0133	-1	1	1	23.4672	-0.0172
25.18	-1	1	2	25.2017	-0.0217					
27.19	0	2	2	27.2178	-0.0278	0	2	1	27.2028	-0.0128
29.4	1	1	2	29.4183	-0.0183					
31.73	-1	1	3	31.7642	-0.0342	1	1	1	31.7349	-0.0049
34.25	0	2	3	34.2853	-0.0353					
35.51	-1	3	1	35.5515	-0.0415	-2	0	1	35.5412	-0.0312
36.88	1	1	3	36.9094	-0.0294	-1	1	2	36.9098	-0.0298
37.13	1	3	1	37.1825	-0.0525	-1	3	1	37.1732	-0.0432
39.61	-1	1	4	39.6086	0.0014					
40.6	0	4	0	40.6416	-0.0416	0	4	0	40.6196	-0.0196
41.07	2	2	0	41.1104	-0.0404					
41.71	0	4	1	41.7383	-0.0283					
42.5	-2	2	2	42.5425	-0.0425	2	2	0	42.5209	-0.0209
43.08	2	0	2	43.1504	-0.0704	-2	0	2	43.1647	-0.0847
43.57	2	2	1	43.6177	0.0477					
44.84	0	4	2	44.8972	-0.0572	0	4	1	44.8723	-0.0323
46.26	-2	2	3	46.3206	-0.0606					
47.18	1	3	3	47.2356	-0.0556	-1	3	2	47.2261	-0.0461
47.94	2	2	2	47.9899	-0.0499	-2	2	2	47.9983	-0.0583
48.24	-1	1	5	48.287	-0.047					
49.75	0	4	3	49.8087	-0.0587					
51.68	-2	2	4	51.7381	-0.0581	2	2	1	51.6937	-0.0137
54.59	-3	1	1	54.6506	-0.0606	-3	1	1	54.6463	-0.0563
55.01	2	4	0	55.0722	-0.0622					
56.16	-2	4	2	56.1446	0.0154	-1	5	1	56.2299	-0.0699
56.94	2	0	4	56.989	-0.049	-2	0	3	57.02	-0.08
58.05	3	1	1	58.1062	-0.0562					
Lattice parameter	a = 5.1307(1)		b = 8.8794(2)	c = 9.8607(2)	β = 100.03(2)°	a = 5.131(1)		b = 8.884(1)	c = 5.147(2)	β =109.3(3)°

* Celref software was used for indexing the PXRD pattern

Table S7: Crystallographic (SCXRD) parameters of Li_4CrSbO_6

Formula	$Li_3Li_{1.01}Cr_{0.985}Sb_{1.0}O_6$
Crystal system	Monoclinic
Space Group	*C2/c*(#15)
***a* [Å]**	5.1368(12)
***b* [Å]**	8.890(2)
***c* [Å]**	9.809(3)
***β* [°]**	99.93(2)
V [Å^3]	441.22(19)
Z	8
Molecular Weight	296.799
***ρ* calc [g/cm^3]**	4.479
Morphology	Irregular
Colour	Light green
Dimensions (mm)	0.14 × 0.08 × 0.05
Temperature [°K]	293(2)
Wavelength [MoK_α][A°]	0.71073
Monochromator	Graphite
Scan mode	ω scan
Min/ Max Bragg angle [°]	4.22 / 28.88
***hkl* range**	-6 → 6, -11 → 12, -12→13
F(000)	540
μ (mm^{-1})	8.526
R_{int}	0.0485
R_{sigma}	0.0345
Absorption Correction	None
Refinement	F^2
No. of unique reflections	544
No. of reflections used	2930
Number of parameters	44
R[F^2 > 2σ(F^2)]	0.0456
wR_2	0.1139
Gof (S)	1.255
Extinction Coefficient	0.0022(7)
Δρ/e[Å^{-3}]	1.534/-0.929

Table S8: Anisotropic Displacement Parameters (SCXRD) of Li_4CrSbO_6

Anisotropic Displacement Parameters (SXRD)						
Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Li1	0.022(8)	0.020(8)	0.016(7)	-0.006(6)	0.002(6)	0.005(5)
Li2	0.032(11)	0.026(11)	0.012(9)	0.005(8)	0.005(8)	-0.006(7)
Li3/Sb1	0.0065(5)	0.0061(5)	0.0056(4)	0	0.0009(3)	0
Li4/Cr1	0.0274(17)	0.037(2)	0.0106(14)	0	0.0015(12)	0
Cr2/Li5/Sb2	0.0033(6)	0.0024(6)	0.0029(6)	0	0.0002(4)	0

Table S9: Selected bond distances for Li_4MSbO_6 (M = Cr, Mn, Ga).

Li_4MSbO_6		M = Cr				M = Mn	*BVS**	M = Ga	*BVS**
Bond Length (Å)		SXRD	*BVS**	PXRD	*BVS**				
Li1	O1	2.154(11)×1		1.930(11)×1		2.084(10)×1		1.891(10) ×1	
		2.186(12)×1		2.239(11)×1		2.618(10)×1		2.291(11) ×1	
	O2	2.138(11)×1		2.315(11)×1		2.030(8)×1		2.027(8) ×1	
		2.191(12)×1		2.101(9)×1		1.821(10)×1		2.030(12) ×1	
	O3	2.137(11)×1	*1.0*	2.255(10)×1	*1.0*	1.965(10)×1	*1.0*	2.366(8) ×1	*1.0*
		2.142(11)×1	0.93	2.109(9)×1	0.965	2.381(7)×1	1.18	2.388(11) ×1	1.034
Li2	O1	2.201(5)×2		2.099(8)×2		2.435(2)×2		2.358(7) ×2	
	O2	2.154(5)×2	*1.0*	2.135(11)×2	*1.0*	2.078(4)×2	*1.0*	1.941(11) ×2	*1.0*
	O3	2.111(5)×2	0.94	2.003(10)×2	1.19	2.061(4)×2	0.93	2.048(11) ×2	1.148
Sb1/Li3	O1	1.997(5)×2		2.121(8)×2		1.769(3)×2		1.842(8) ×2	
	O2	1.991(5)×2	*4.0*	1.846(11)×2	*4.52*#	1.985(4)×2	*4.46*	2.154(12) ×2	*4.76*
	O3	1.996(5)×2	4.26	1.859(10)×2	5.25#	2.154(4)×2	5.50	2.004(10) ×2	5.204
Li4/M1	O1	2.060(5)×2		2.294(13)×2		2.460(6)×2		2.101(14) ×2	
	O2	2.086(5)×2	*2.06*	2.113(9)×2	*1.78*#	1.985(3)×2	*1.326*	2.039(8) ×2	*1.26*
	O3	2.105(5)×2	1.74	2.239(12)×2	1.09#	2.008(6)×2	1.30	2.212(15) ×2	1.194
M2/Sb3/Li5	O1	2.041(5)×2		1.962(11)×2		2.050(4)×2		2.015(11) ×2	
	O2	2.020(5)×2	*2.9*	2.081(11)×2	*3.1*	2.099(4)×2	*3.033*	2.238(11) ×2	*2.94*
	O3	2.044(5)×2	2.72	2.106(10)×2	2.65	2.093(3)×2	1.90	1.970(8) ×2	2.467

* Expected BVS are shown in italics; # Difference possibly arising out of stacking faults.

Table S10: Cell Parameters (Space Group $P3_112$) of $Ag_3LiMSbO_6$ (M = Cr, Fe, Al, Ga) obtained from PXRD.

Compound	***a* (Å)**	***c* (Å)**
$Ag_3LiCrSbO_6$	5.27(1)	18.63(6)
$Ag_3LiFeSbO_6$	5.33(8)	18.77(2)
$Ag_3LiAlSbO_6$	5.27(1)	18.65(6)
$Ag_3LiGaSbO_6$	5.287(0)	18.774(1)

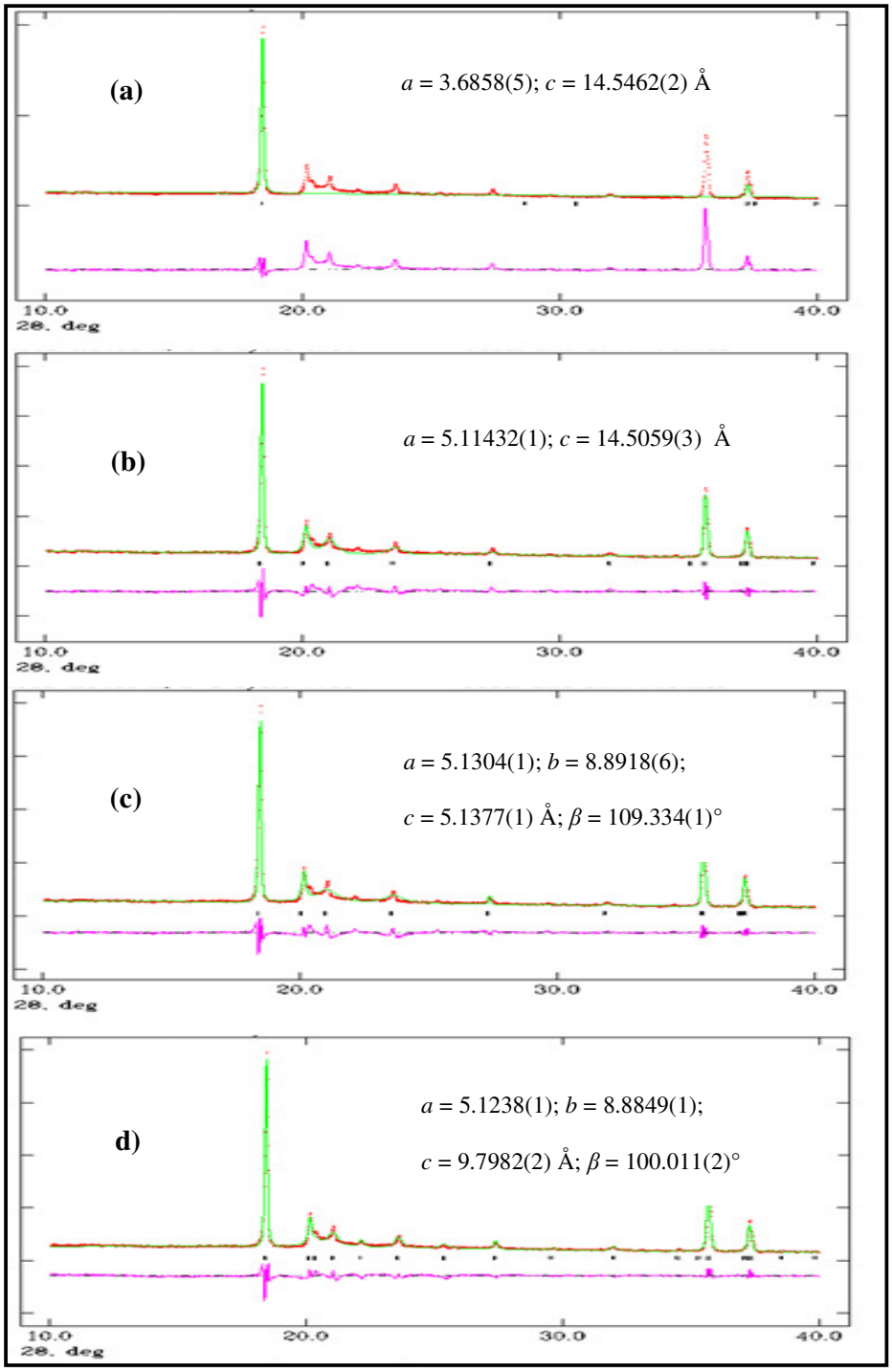


Fig. S1. Powder X-Ray diffraction pattern of Li_4CrSbO_6 indexed using (a) *R-3m* subcell, (b) *P3₁12* supercell, (c) *C2/m* supercell, and (d) *C2/c* supercell; Red line experimental data; green line calculated profile; pink line difference profile; vertical bars, Bragg positions.

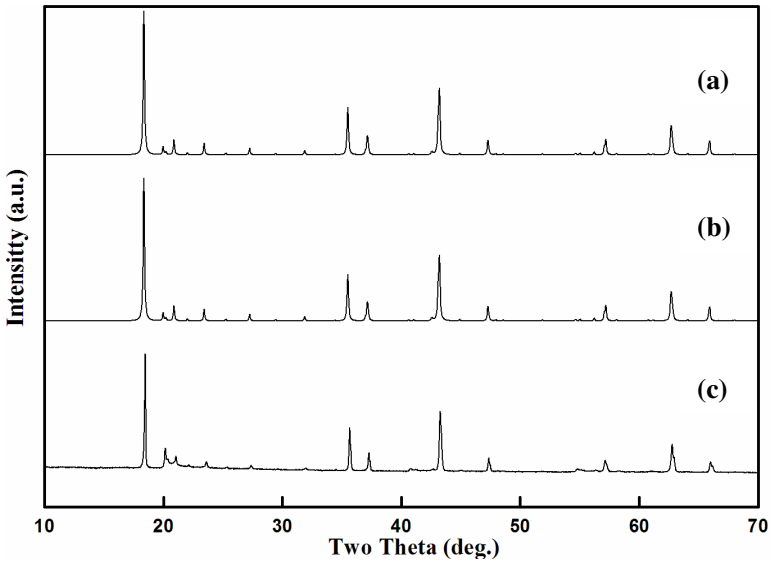
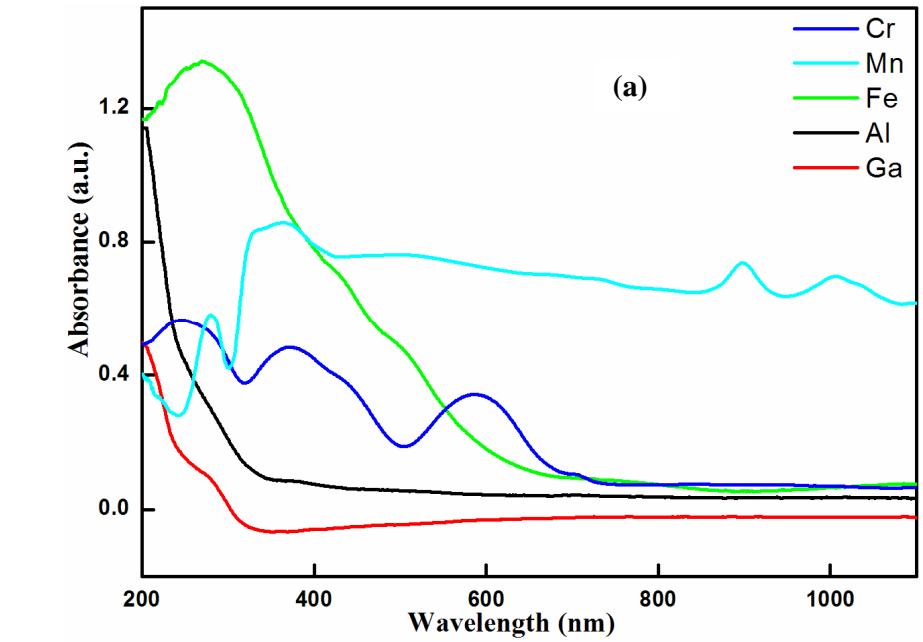


Fig. S2 (a) PXRD plot derived from the measured SCXRD intensities for Li_4CrSbO_6; **(b)** simulated PXRD pattern using the SCXRD solution of Li_4CrSbO_6; **(c)** PXRD pattern obtained for the bulk polycrystalline Li_4CrSbO_6.



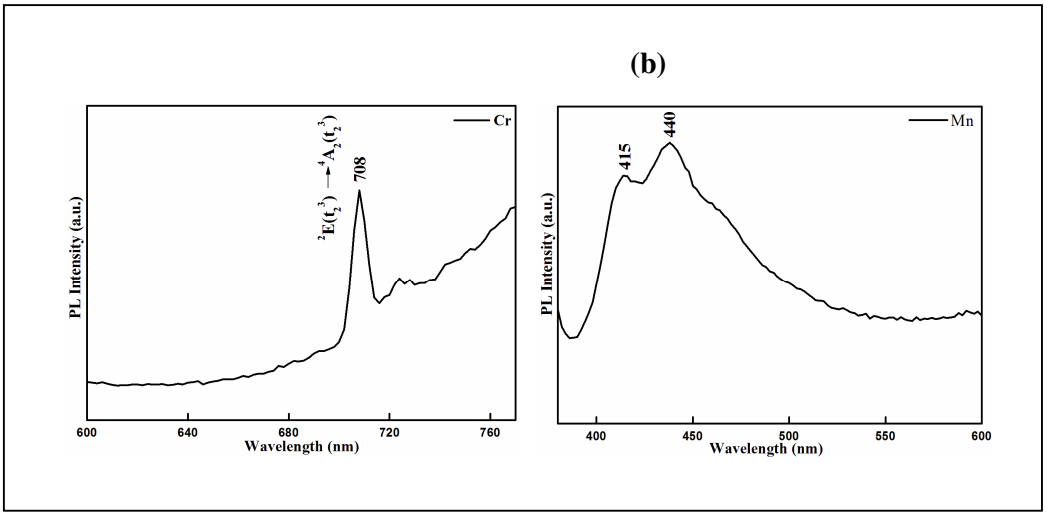


Fig. S3 (a) Diffuse reflectance spectra of Li_4MSbO_6 (M = Cr, Mn, Fe, Al, Ga) and **(b)** Photoluminescence spectra of Li_4CrSbO_6 and Li_4MnSbO_6.

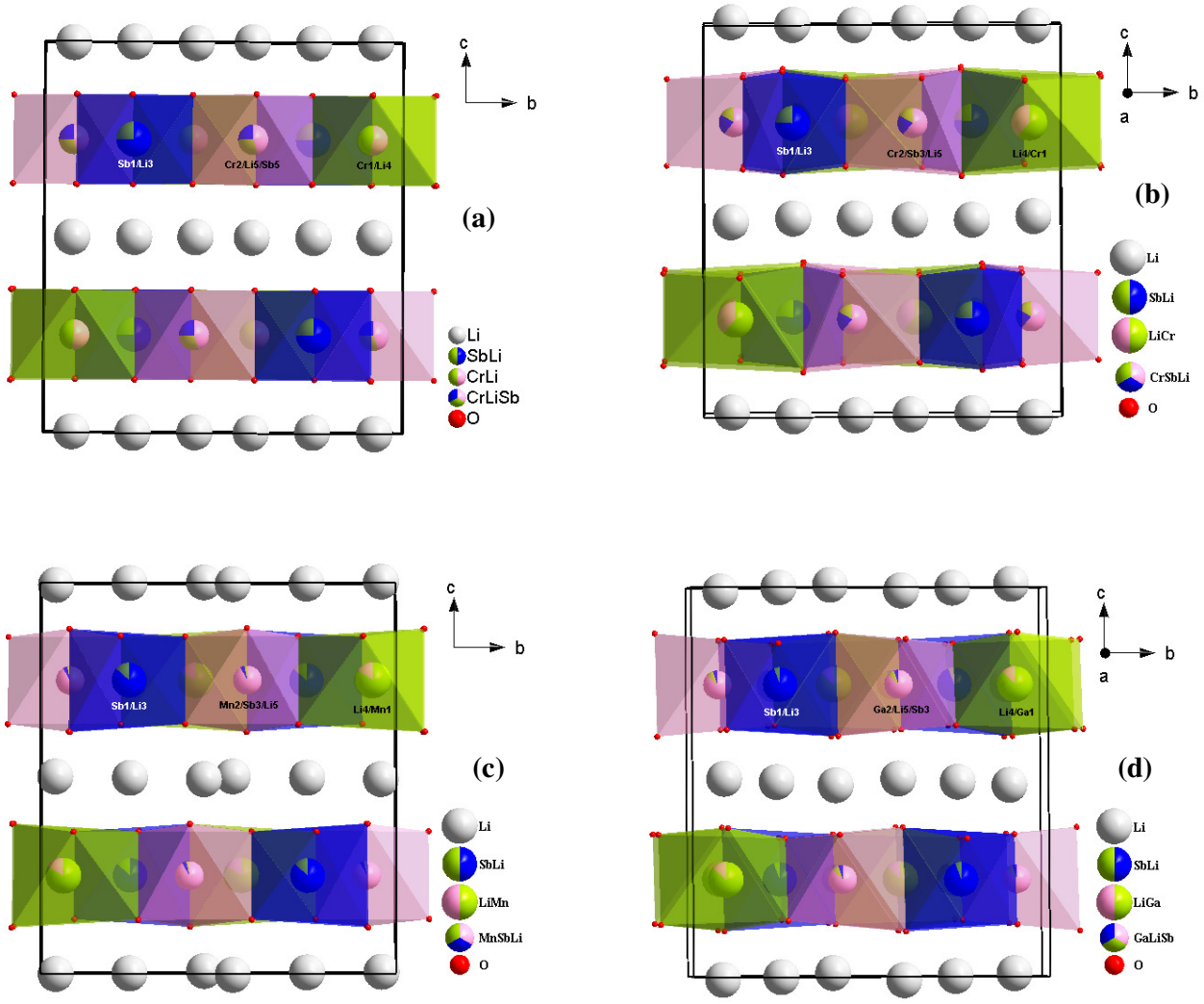


Fig. S4 Structure of Li_4MSbO_6 (M = **(a)** Cr (SCXRD), **(b)** Cr (PXRD), **(c)** Mn, **(d)** Ga) perpendicular to the honeycomb layers.

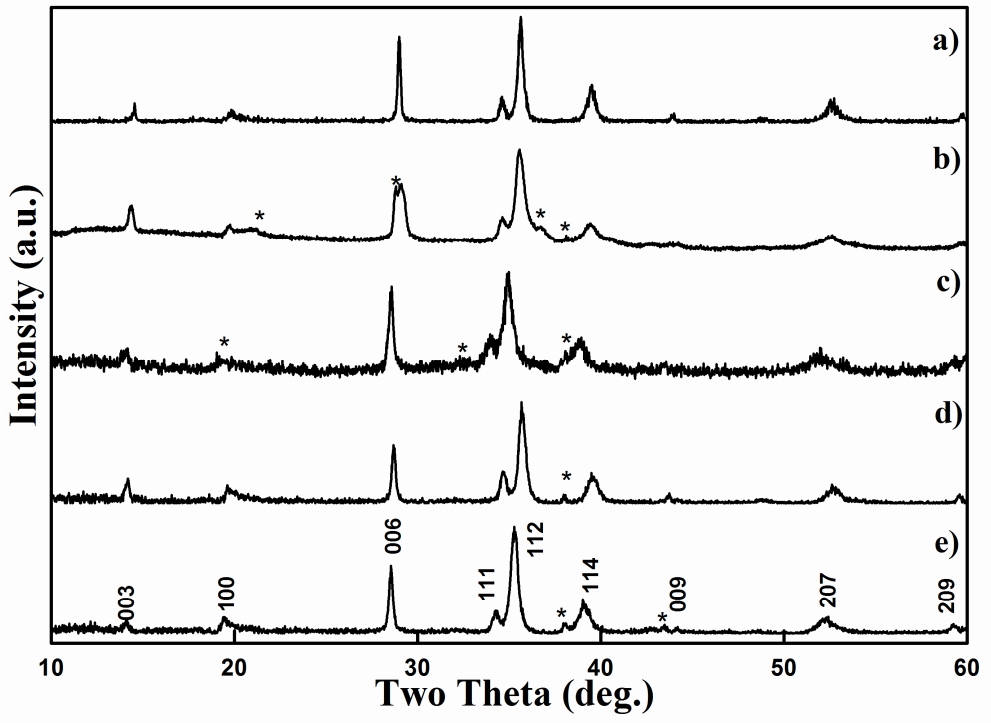


Fig. S5 PXRD patterns of $Ag_3LiMSbO_6$ for M = **(a)** Cr, **(b)** Mn, **(c)** Fe, **(d)** Al, **(e)** Ga.

(* represents parent oxide).

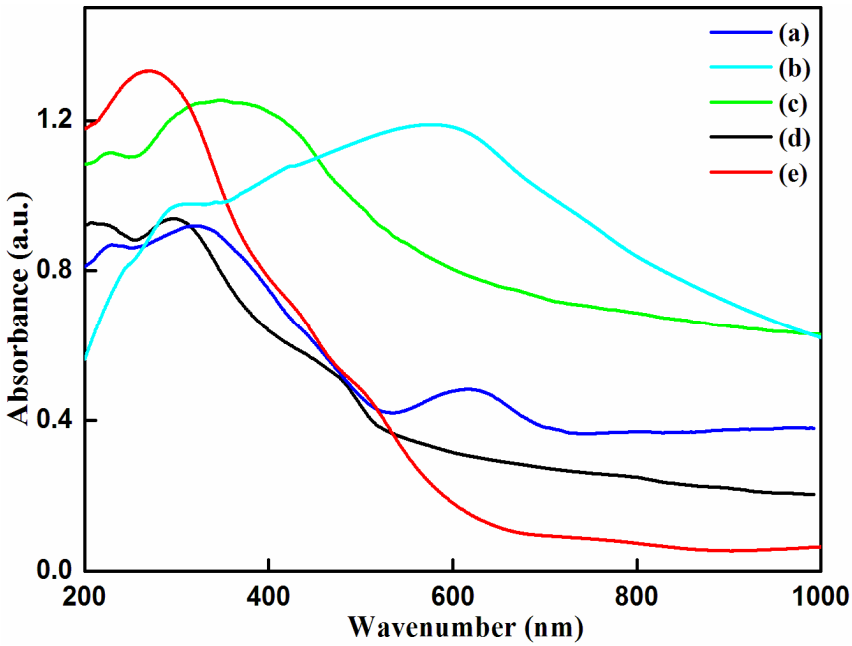


Fig. S6 Diffuse reflectance spectra of $Ag_3LiMSbO_6$ (M = **(a)** Cr, **(b)** Fe, **(c)** Mn, **(d)** Al, **(e)** Ga).

REFERENCES

[1] J. C. Anderson and M. Schirber, *J. Phys. Chem. Solids*, 1964, **25**, 961.

[2] B. Fuchs and S. Kemmler-Sack *Solid State Ionics*, 1994, **68**, 279.

[3] M. Castellanos, A. R. West and W. B. Reid, *Acta Cryst*., 1985, **C4**, 1707.

[4] M. Castellanos and A. R. West, *J. Mater. Sci*., 1979, **14**, 450.

[5] V. Massarotti, M. Bini, D. Capsoni, A. Altomare and A. G. G. Moliterni, *J. Appl. Cryst*., 1997, **30**, 123.

[6] Y. Miura, Y. Yasui, M. Sato, N. Igawa1 and K. Kakurai, *J. Phys. Soc. Jpn*., 2007, **76**, 33705.

[7] A. Alexander, P. D. Battle, J. C. Burley, D. J. Gallon, C. P. Grey and S. H. Kim, *J. Mater. Chem*., 2003, **13**, 2612.

[8] S. Vensky, L. Kienle, R. E. Dinnebier, A. S. Masadeh, S. J. .Billinge and M. Jansen, *Z. Kristallogr*., 2005, **220**, 231.

[9] L. R. Morss, E. H. Appelman, R. R. Gerz and D. Martin-Rovet, *J. Alloys Comp*., 1994, **203**, 289.

[10] E. A. Zvereva, M. A. Evstigneeva, V. B. Nalbandyan, O. A. Savelieva, S. A. Ibragimov, O. S. Volkova, L. I. Medvedeva, A. N. Vasiliev, R. Klingeler and B. Buechner, *Dalton Trans*., 2012, **41**, 572.

[11] J. M. S. Skakle, R. M. A. Castellanos, S. T. Tovar and A. R. West, *J. Solid StateChem*., 1997, **131**, 115.

[12] C. Greaves and S. M. A. Katib, *Mater. Res. Bull*., 1990, **25**, 1175.

[13] R. Berthelot, W. Schmidt, S. Muir, J. Eilertsen, L. Etienne, A. W. Sleight and M.A. Subramanian, *Inorg. Chem*., 2012, **51**, 5377.

[14] W. Schmidt, R. Berthelot, A.W. Sleight and M.A. Subramanian, *J. Solid State Chem.* 2013, **201**, 178.

[15] L. Viciu, Q. Huang, E. Morosan, H. W. Zandbergen, N. I. Greenbaum, T. McQueen and R. J. Cava, *J. Solid State Chem*., 2007, **180**, 1060; V. V. Politaev, V. B. Nalbandyan, A. A. Petrenko, I. L. Shukaev, V. A.Volotchaev, B. S. Medvedev, *J. Solid State Chem*., 2010, **183**, 684.

[16] V. Kumar, A. Gupta and S. Uma, *Dalton Trans*., 2013, **42**, 14992.

[17] M. A. Evstigneeva, V. B. Nalbandyan, A. A. Petrenko, B. S. Medvedeva and A. A. Kataev, *Chem. Mater*., 2011, **23**, 1174.

[18] J. Xu, A. Assoud, N. Soheilnia, S. Derakhshan, H. L. Cuthbert, J. E. Greedan, M. H. Whangbo and H. Kleinke, *Inorg. Chem*., 2005, **44**, 5042.

[19] W. Schmidt, R. Berthelot, L. Etienne, A. Wattiaux and M. A. Subramanian, *Mater. Res. Bull.*, 2014, **50**, 292.

[20] E. A. Zvereva, O. A. Savelieva, Ya. D. Titov, M. A. Evstigneeva, V. B. Nalbandyan, C. N. Kao, J. -Y. Lin, I. A. Presniakov, A. V. Sobolev, S. A. Ibragimov, M. Abdel-Hafiez, Yu. Krupskaya, C. Jähne, G. Tan, R. Klingeler, B. Büchner and A. N. Vasiliev, *Dalton Trans*., 2013, **42**, 1550.

[21] V. Kumar, N. Bhardwaj, N.Tomar, V.Thakral and S. Uma, *Inorg. Chem*., 2012, **51**, 10471.