Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplmenetary Information

High-throughput investigation of the formation of double spinels

V. Kocevski, G. Pilania, and B. P. Uberuaga
Materials Science and Technology Division, Los Alamos National Laboratory, Los Alamos, NM 87545, USA

Table. S1. Total energy (E_{tot}), in eV/formula unit, of the experimentally (expr.) determined normal (left) and inverse (right) spinels, along with the energy of the compound in the other structural type.

	Expr. normal			Expr. Inverse	
Composition	Normal E_{tot}	Inverse E_{tot}	Composition	Inverse E_{tot}	Normal E_{tot}
$CdCr_2O_4$	-47.621	-45.616	Al_2CdO_4*	-44.367	-45.064
$CdFe_2O_4$	-41.137	-40.763	Al_2NiO_4	-47.119	-46.815
$CdGa_2O_4$	-37.756	-37.230	Cd_2GeO_4	-35.049	-34.737
$CdIn_2O_4$	-35.852	-35.283	Co_2CuO_4*	-39.609	-39.806
$CdMn_2O_4$	-45.414	-44.797	Co_2FeO_4	-44.018	-43.680
$CdRh_2O_4$	-40.961	-38.949	Co_2MnO_4	-46.024	-45.590
CdV_2O_4	-47.881	-46.934	Co_2NiO_4	-39.444	-39.343
$CoAl_2O_4$	-49.884	-49.557	Fe_2CoO_4	-45.677	-45.626
$CoCo_2O_4$	-42.490	-42.121	Fe_2CuO_4	-42.769	-42.704
$CoCr_2O_4$	-52.079	-50.466	Fe_2FeO_4	-46.684	-46.684
$CoMn_2O_4$	-49.665	-49.485	Fe_2MgO_4	-45.402	-45.324
$CoRh_2O_4$	-45.192	-43.796	Fe_2NiO_4	-43.056	-42.309
CoV_2O_4	-52.339	-51.646	Ga_2CoO_4	-42.211	-42.137
$CuAl_2O_4$	-46.898	-46.697	Ga_2CuO_4	-39.279	-39.222
$CuCr_2O_4$	-49.198	-47.872	Ga_2MgO_4	-42.058	-41.979
$CuMn_2O_4$	-47.207	-46.858	Ga_2NiO_4	-39.659	-39.112
$CuRh_2O_4$	-42.866	-41.499	Ge_2FeO_4*	-46.060	-46.227
$FeAl_2O_4$	-50.785	-50.557	In_2MgO_4	-39.621	-39.535
$FeCr_2O_4$	-53.051	-51.684	Mn_2FeO_4	-51.201	-50.986
FeV_2O_4	-53.230	-52.799	Mn_2NiO_4	-47.012	-46.400
$GeCo_2O_4$*	-43.800	-43.942	Sn_2ZnO_4	-37.959	-37.322
$GeFe_2O_4$	-46.227	-46.060	Zn_2GeO_4	-37.336	-36.919
$GeMg_2O_4$	-43.653	-43.560			
$GeNi_2O_4$	-38.774	-38.377			
$MgAl_2O_4$	-49.678	-49.487			
$MgCo_2O_4$	-42.055	-41.548			
$MgCr_2O_4$	-51.791	-50.315			
$MgMn_2O_4$	-49.544	-49.403			
$MgRh_2O_4$	-44.759	-43.509			
$MgTi_2O_4$	-56.702	-56.213			
MgV_2O_4	-51.986	-51.547			
$MnAl_2O_4$	-53.202	-52.737			
$MnCr_2O_4$	-55.539	-53.928			
$MnFe_2O_4$	-49.285	-49.048			

$MnGa_2O_4$	-45.685	-45.440
$MnMn_2O_4$	-53.328	-53.327
$MnRh_2O_4$	-48.697	-47.297
$MnTi_2O_4$	-60.468	-59.937
MnV_2O_4	-55.804	-55.128
$NiCr_2O_4$	-48.853	-47.903
$NiRh_2O_4$	-42.010	-41.123
$ZnAl_2O_4$	-46.786	-46.100
$ZnCr_2O_4$	-48.889	-47.023
$ZnFe_2O_4$	-42.421	-42.085
$ZnGa_2O_4$	-39.092	-38.715
$ZnIn_2O_4$	-36.579	-36.377
$ZnMn_2O_4$	-46.619	-46.097
$ZnRh_2O_4$	-41.949	-40.208
ZnV_2O_4	-49.093	-48.224

*Single spinel where the calculations predict a different ground state structure than experimentally reported.

Table. S2. Mixing enthalpies (E_{mix}), in eV/formula unit, of the considered double spinels with three different types, in ascending order of the lowest E_{mix}. The single spinels that can form the double spinels, the composition of the lowest energy type and the type that they can form. In parenthesis is the cation in tetrahedral site.

Reference single spinels		Lowest energy			E_{mix} (eV/ formula unit)		
Normal	Inverse	Composition	Type	E_{mix}	DS-Inv_1	DS-Norm	DS-Inv_2
$MgTi_2O_4$	In_2MgO_4	(In)$TiMgO_4$	DS-Inv_1	-2.5479	-2.5479	0.3437	-2.0670
$MnTi_2O_4$	Co_2MnO_4	(Mn)$TiCoO_4$	DS-Norm	-1.4981	-1.3626	-1.4981	-1.3724
$MgTi_2O_4$	Fe_2MgO_4	(Ti)$FeMgO_4$	DS-Inv_2	-1.1102	-1.0422	-0.9445	-1.1102
$ZnMn_2O_4$	Sn_2ZnO_4	(Zn)$MnSnO_4$	DS-Norm	-0.9257	-0.3312	-0.9257	-0.9213
$ZnFe_2O_4$	Sn_2ZnO_4	(Zn)$FeSnO_4$	DS-Norm	-0.7303	-0.0615	-0.7303	-0.4832
$ZnIn_2O_4$	Sn_2ZnO_4	(In)$SnZnO_4$	DS-Inv_2	-0.4686	-0.2966	0.3402	-0.4686
$NiRh_2O_4$	Co_2NiO_4	(Co)$RhNiO_4$	DS-Inv_1	-0.4384	-0.4384	0.0764	1.2278
$FeAl_2O_4$	Co_2FeO_4	(Co)$AlFeO_4$*	DS-Inv_1	-0.3485	-0.3485	-0.1827	0.0496
FeV_2O_4	Co_2FeO_4	(Co)$VFeO_4$*	DS-Inv_1	-0.3452	-0.3452	0.2075	-0.2071
$FeCr_2O_4$	Co_2FeO_4	(Co)$CrFeO_4$*	DS-Inv_1	-0.3371	-0.3371	-0.1539	1.2025
FeV_2O_4	Mn_2FeO_4	(Mn)$VFeO_4$	DS-Inv_1	-0.3238	-0.3238	-0.0903	0.3787
$FeCr_2O_4$	Mn_2FeO_4	(Mn)$CrFeO_4$	DS-Inv_1	-0.3186	-0.3186	0.0067	1.3370
$NiCr_2O_4$	Ga_2NiO_4	(Ga)$CrNiO_4$	DS-Inv_1	-0.2801	-0.2801	0.2507	1.2677
$FeAl_2O_4$	Mn_2FeO_4	(Mn)$AlFeO_4$	DS-Inv_1	-0.2512	-0.2512	0.0402	0.3002
$GeNi_2O_4$	Zn_2GeO_4	(Zn)$NiGeO_4$	DS-Inv_1	-0.2169	-0.2169	0.2199	0.6288
$CdRh_2O_4$	Al_2CdO_4	(Cd)$RhAlO_4$	DS-Norm	-0.1939	0.8844	-0.1939	1.4108
MgV_2O_4	In_2MgO_4	(In)$VMgO_4$	DS-Inv_1	-0.1877	-0.1877	0.1405	0.3357
MnV_2O_4	Co_2MnO_4	(Mn)$VCoO_4$	DS-Norm	-0.1862	-0.1630	-0.1862	0.2190
$NiCr_2O_4$	Co_2NiO_4	(Co)$CrNiO_4$	DS-Inv_1	-0.1847	-0.1847	0.0592	0.7692
$NiRh_2O_4$	Mn_2NiO_4	(Mn)$RhNiO_4$	DS-Inv_1	-0.1819	-0.1819	0.1958	1.4819
$NiCr_2O_4$	Fe_2NiO_4	(Fe)$CrNiO_4$	DS-Inv_1	-0.1759	-0.1759	0.2420	1.1736
$CuRh_2O_4$	Ga_2CuO_4	(Cu)$RhGaO_4$	DS-Norm	-0.1653	0.4121	-0.1653	1.8689
$NiRh_2O_4$	Ga_2NiO_4	(Ga)$RhNiO_4$	DS-Inv_1	-0.1604	-0.1604	0.1752	1.9498

$CuRh_2O_4$	Fe_2CuO_4	$(Cu)RhFeO_4$	DS-Norm	-0.1524	0.4419	-0.1524	1.6854
$MnRh_2O_4$	Co_2MnO_4	$(Co)RhMnO_4$	DS-Inv$_1$	-0.1471	-0.1471	0.0550	1.5548
$GeMg_2O_4$	Zn_2GeO_4	$(Zn)MgGeO_4$	DS-Inv$_1$	-0.1384	-0.1384	0.1742	0.2133
$CoRh_2O_4$	Fe_2CoO_4	$(Co)RhFeO_4$	DS-Norm	-0.1340	0.2240	-0.1340	1.9256
$GeCo_2O_4$	Zn_2GeO_4	$(Zn)CoGeO_4$	DS-Inv$_1$	-0.1274	-0.1274	0.2810	0.1505
$MgRh_2O_4$	Ga_2MgO_4	$(Ga)RhMgO_4$	DS-Inv$_1$	-0.1220	-0.1220	-0.1077	2.0432
$NiRh_2O_4$	Fe_2NiO_4	$(Fe)RhNiO_4$	DS-Inv$_1$	-0.1199	-0.1199	0.1495	1.7222
$CoRh_2O_4$	Ga_2CoO_4	$(Co)RhGaO_4$	DS-Norm	-0.1160	0.2056	-0.1160	2.0488
MgV_2O_4	Ga_2MgO_4	$(Ga)VMgO_4$	DS-Inv$_1$	-0.1003	-0.1003	0.0935	0.5836
$MnAl_2O_4$	Co_2MnO_4	$(Co)AlMnO_4$	DS-Inv$_1$	-0.0969	-0.0969	0.0888	0.2869
$CuMn_2O_4$	Co_2CuO_4	$(Cu)MnCoO_4$	DS-Norm	-0.0904	0.2101	-0.0904	0.3753
$MgAl_2O_4$	Ga_2MgO_4	$(Ga)AlMgO_4$	DS-Inv$_1$	-0.0861	-0.0861	0.0685	0.3148
$CuAl_2O_4$	Ga_2CuO_4	$(Ga)AlCuO_4$	DS-Inv$_1$	-0.0846	-0.0846	0.0631	0.3330
$CuRh_2O_4$	Co_2CuO_4	$(Cu)RhCoO_4$	DS-Norm	-0.0843	0.0267	-0.0843	1.4552
$MgRh_2O_4$	Fe_2MgO_4	$(Mg)RhFeO_4$	DS-Norm	-0.0784	-0.0063	-0.0784	1.9579
$NiCr_2O_4$	Al_2NiO_4	$(Al)CrNiO_4$	DS-Inv$_1$	-0.0739	-0.0739	0.1201	1.1487
$CdCr_2O_4$	Al_2CdO_4	$(Cd)CrAlO_4$	DS-Norm	-0.0674	0.7269	-0.0674	1.8579
$MgRh_2O_4$	In_2MgO_4	$(In)RhMgO_4$	DS-Inv$_1$	-0.0660	-0.0660	1.4595	0.0197
$MgMn_2O_4$	In_2MgO_4	$(In)MnMgO_4$	DS-Inv$_1$	-0.0627	-0.0627	0.2694	0.9532
$MnCr_2O_4$	Co_2MnO_4	$(Co)CrMnO_4$	DS-Inv$_1$	-0.0619	-0.0619	0.1791	1.2718
$CuMn_2O_4$	Fe_2CuO_4	$(Cu)MnFeO_4$	DS-Norm	-0.0579	0.0841	-0.0579	0.1874
$GeFe_2O_4$	Cd_2GeO_4	$(Cd)FeGeO_4$	DS-Inv$_1$	-0.0544	-0.0544	0.2014	0.4079
$GeCo_2O_4$	Cd_2GeO_4	$(Cd)CoGeO_4$	DS-Inv$_1$	-0.0512	-0.0512	0.3805	0.4768
$GeNi_2O_4$	Cd_2GeO_4	$(Cd)NiGeO_4$	DS-Inv$_1$	-0.0511	-0.0511	0.4049	0.9373
$CdFe_2O_4$	Al_2CdO_4	$(Cd)FeAlO_4$	DS-Norm	-0.0475	0.6485	-0.0475	0.5725
$MgCr_2O_4$	Ga_2MgO_4	$(Ga)CrMgO_4$	DS-Inv$_1$	-0.0407	-0.0407	0.0502	0.8797
$CuMn_2O_4$	Ga_2CuO_4	$(Cu)MnGaO_4$	DS-Norm	-0.0343	0.0746	-0.0343	0.2159
$GeMg_2O_4$	Cd_2GeO_4	$(Cd)MgGeO_4$	DS-Inv$_1$	-0.0177	-0.0177	0.3267	0.4832
$MnGa_2O_4$	Co_2MnO_4	$(Co)GaMnO_4$*	DS-Inv$_1$	-0.0145	-0.0145	0.1404	0.0252
$CuAl_2O_4$	Co_2CuO_4	$(Cu)AlCoO_4$	DS-Norm	-0.0140	0.0515	-0.0140	0.7146
$MnFe_2O_4$	Co_2MnO_4	$(Co)MnFeO_4$*	DS-Inv$_1$	-0.0065	-0.0065	0.1932	0.1751
$CdGa_2O_4$	Al_2CdO_4	$(Cd)GaAlO_4$	DS-Norm	0.0042	0.7665	0.0042	0.4745
$CoAl_2O_4$	Ga_2CoO_4	$(Ga)AlCoO_4$	DS-Inv$_1$	0.0045	0.0045	0.0301	0.4419
$GeFe_2O_4$	Zn_2GeO_4	$(Zn)FeGeO_4$	DS-Inv$_1$	0.0057	0.0057	0.2080	0.2218
$CoCr_2O_4$	Fe_2CoO_4	$(Co)CrFeO_4$*	DS-Norm	0.0064	0.1896	0.0064	1.5106
$CoMn_2O_4$	Fe_2CoO_4	$(Co)MnFeO_4$*	DS-Norm	0.0100	0.1359	0.0100	0.2097
$CoCr_2O_4$	Ga_2CoO_4	$(Co)CrGaO_4$	DS-Norm	0.0138	0.1055	0.0138	1.6235
MgV_2O_4	Fe_2MgO_4	$(Mg)VFeO_4$	DS-Norm	0.0146	0.0573	0.0146	0.4309
$NiRh_2O_4$	Al_2NiO_4	$(Ni)RhAlO_4$	DS-Norm	0.0162	0.1416	0.0162	1.8848
$MgCr_2O_4$	Fe_2MgO_4	$(Mg)CrFeO_4$	DS-Norm	0.0194	0.1136	0.0194	1.4385
$CdMn_2O_4$	Al_2CdO_4	$(Cd)MnAlO_4$	DS-Norm	0.0286	0.7582	0.0286	1.1452
$CoAl_2O_4$	Fe_2CoO_4	$(Co)AlFeO_4$*	DS-Norm	0.0305	0.1963	0.0305	0.4492
$CuCr_2O_4$	Fe_2CuO_4	$(Cu)CrFeO_4$	DS-Norm	0.0316	0.2038	0.0316	1.2665
$CoMn_2O_4$	Ga_2CoO_4	$(Co)GaMnO_4$*	DS-Norm	0.0329	0.1089	0.0329	0.2242
$MgCo_2O_4$	Ga_2MgO_4	$(Ga)CoMgO_4$	DS-Inv$_1$	0.0356	0.0356	0.2475	0.5215
CoV_2O_4	Ga_2CoO_4	$(Ga)VCoO_4$	DS-Inv$_1$	0.0389	0.0389	0.0793	0.6971
CoV_2O_4	Fe_2CoO_4	$(Co)VFeO_4$*	DS-Norm	0.0397	0.1518	0.0397	0.5915
$CuAl_2O_4$	Fe_2CuO_4	$(Cu)AlFeO_4$	DS-Norm	0.0417	0.0988	0.0417	0.3793

$CuCr_2O_4$	Ga_2CuO_4	$(Cu)CrGaO_4$	DS-Norm	0.0439	0.1029	0.0439	1.3750
$MgCr_2O_4$	In_2MgO_4	$(In)CrMgO_4$	DS-Inv_1	0.0506	0.0506	0.1606	1.6992
$CdIn_2O_4$	Al_2CdO_4	$(Cd)InAlO_4$	DS-Norm	0.0559	0.7791	0.0559	0.5007
$CuCr_2O_4$	Co_2CuO_4	$(Cu)CrCoO_4$	DS-Norm	0.0564	0.1173	0.0564	1.1591
$MgMn_2O_4$	Ga_2MgO_4	$(Ga)MnMgO_4$	DS-Inv_1	0.0641	0.0641	0.1795	0.8513
$MgAl_2O_4$	Fe_2MgO_4	$(Mg)AlFeO_4$	DS-Norm	0.0735	0.1791	0.0735	0.2850
$MgAl_2O_4$	In_2MgO_4	$(In)AlMgO_4$	DS-Inv_1	0.0869	0.0869	0.2521	0.5007
$MgTi_2O_4$	Ga_2MgO_4	$(Ga)TiMgO_4$	DS-Inv_1	0.0989	0.0989	0.2926	0.8843
$MgMn_2O_4$	Fe_2MgO_4	$(Mg)MnFeO_4$	DS-Norm	0.1281	0.1335	0.1281	0.7210
ZnV_2O_4	Sn_2ZnO_4	$(Zn)VSnO_4$	DS-Norm	0.1285	0.6630	0.1285	1.1823
$MgCo_2O_4$	Fe_2MgO_4	$(Mg)CoFeO_4$	DS-Norm	0.1392	0.2615	0.1392	0.2850
$ZnRh_2O_4$	Sn_2ZnO_4	$(Zn)RhSnO_4$	DS-Norm	0.2668	0.3802	0.2668	1.2355
$MgCo_2O_4$	In_2MgO_4	$(In)CoMgO_4$	DS-Inv_1	0.2693	0.2693	0.3013	0.8027
$NiCr_2O_4$	Mn_2NiO_4	$(Ni)CrMnO_4$	DS-Norm	0.2766	0.3623	0.2766	1.0442
$ZnCr_2O_4$	Sn_2ZnO_4	$(Zn)CrSnO_4$	DS-Norm	0.4610	0.6684	0.4610	0.9382
$ZnGa_2O_4$	Sn_2ZnO_4	$(Sn)GaZnO_4$	DS-Inv_1	0.6737	0.6737	0.6985	0.9087
$ZnAl_2O_4$	Sn_2ZnO_4	$(Sn)AlZnO_4$	DS-Inv_1	0.8791	0.8791	0.9545	1.5088
CdV_2O_4	Al_2CdO_4	$(Cd)VAlO_4$	DS-Norm	0.9003	1.5339	0.9003	1.9242
FeV_2O_4	Ge_2FeO_4	$(Ge)VFeO_4$	DS-Inv_1	0.9904	0.9904	1.1672	2.4722
$FeCr_2O_4$	Ge_2FeO_4	$(Ge)CrFeO_4$	DS-Inv_1	1.3604	1.3604	1.5721	1.7258
$FeAl_2O_4$	Ge_2FeO_4	$(Fe)AlGeO_4$	DS-Norm	1.7070	2.0412	1.7070	2.1582

*Double spinels with same composition, but can be made from different single spinels

Table. S3. List of single spinels for which other structure type (other phase) is reported to be more stable, with their space group, and total energy of the other phase and the spinel. The three last columns on the right show the reevaluated E_{mix} using the energy of the more stable other phase.

		E_{tot} (eV/formula unit)		Reevaluated E_{mix} (eV/formula unit)		
Composition	Space group	Other phase	Spinel	DS-Inv_1	DS-Norm	DS-Inv_2
Zn_2GeO_4	R-3	**-37.493**	-37.336	**-0.0487**	0.3597	0.2292
				0.0844	0.2867	0.3005
				-0.0597	0.2529	0.2920
				-0.1382	0.2986	0.7075
Cd_2GeO_4	Pnma	**-35.417**	-35.049	0.1329	0.5646	0.6609
				0.1297	0.3854	0.5920
				0.1664	0.5108	0.6673
				0.1330	0.5890	1.1213
$ZnIn_2O_4$	Pnma	-36.334	**-36.579**			
$ZnIn_2O_4$	P21/c	-36.574	**-36.579**			
$GeMg_2O_4$	Pnma	-43.649	**-43.653**			
Cr_2FeO_4	Pnma	-52.510	**-53.051**			
Fe_2MgO_4	Imma	-44.645	**-45.402**			

Table. S4. Relative stability, i.e., distance from convex hull (E in eV) for the single spinels that form the same double spinel structure with different type, taken from Materials Project [1].

DS-Inv_1				DS-Inv_2			
Normal	E (eV)	Inverse	E (eV)	Normal	E (eV)	Inverse	E (eV)
Al_2FeO_4	0.137	Co_2FeO	0.037	Al_2CoO_4	0	Fe_2CoO_4	0
V_2FeO_4	0.099	Co_2FeO_4	0.037	V_2CoO_4	0	Fe_2CoO_4	0
Cr_2FeO_4	0.139	Co_2FeO_4	0.037	Cr_2CoO_4	0	Fe_2CoO_4	0
Ga_2MnO_4	no data	Co_2MnO_4	0.202	Mn_2CoO_4	0.006	Ga_2CoO_4	0
Fe_2MnO_4	0	Co_2MnO_4	0.202	Mn_2CoO_4	0.006	Fe_2CoO_4	0

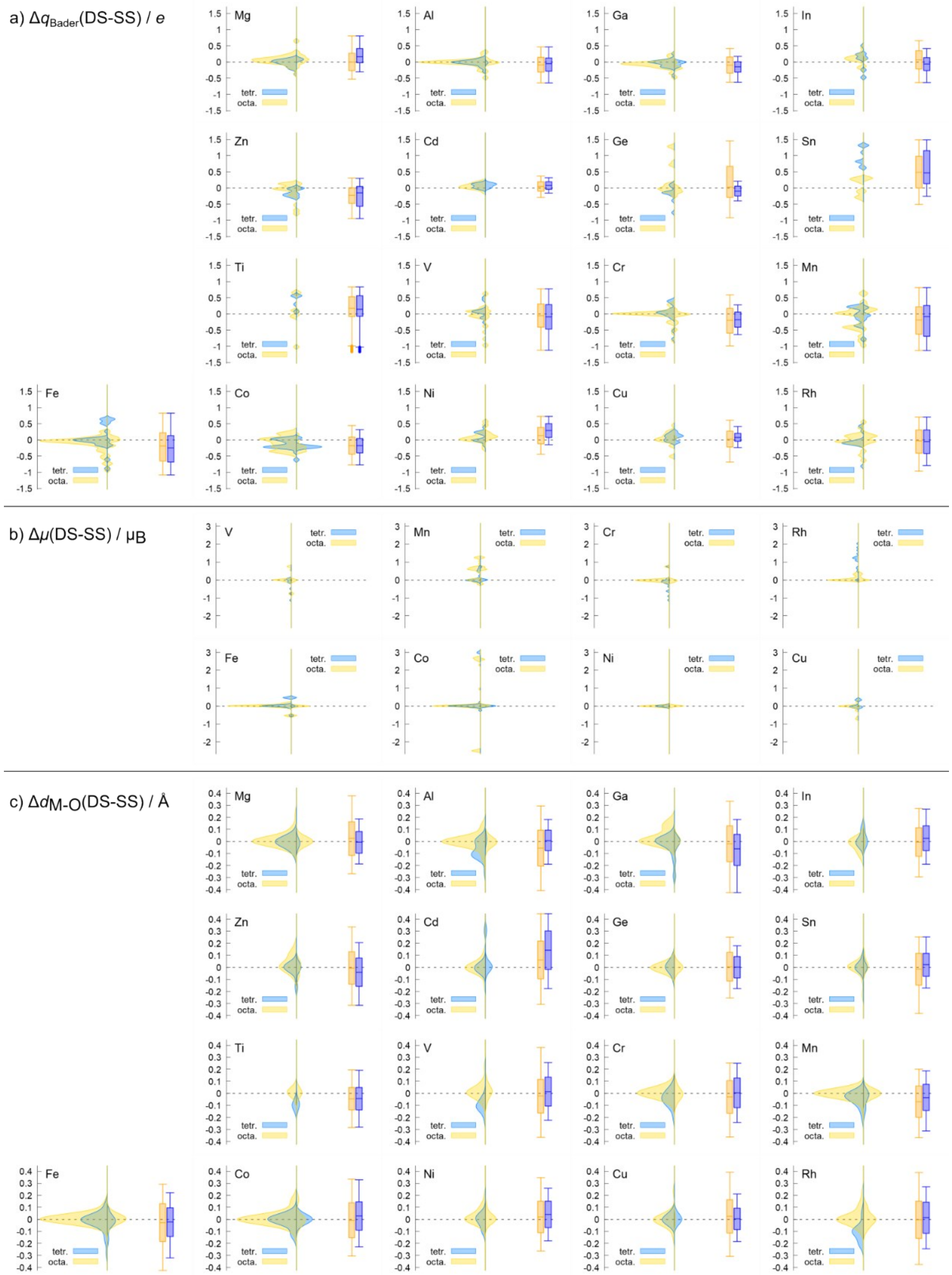

Fig. S1. Violin plots showing the distribution of the: a) Bader charge (Δq_{bader}), b) magnetic moment ($\Delta\mu$), and c) cation–oxygen distance ($\Delta d_{M\text{-}O}$) difference in the double spinel (DS) and the reference single spinels (SS) for all cations. The cation site, tetrahedral and octahedral is shown in blue and yellow, respectively. The distribution in all spinels and only in the stable spinels is shown in the left and right part of the violin plot, respectively. The box-plots for the total number and stable double spinels are shown in orange and purple, respectively.

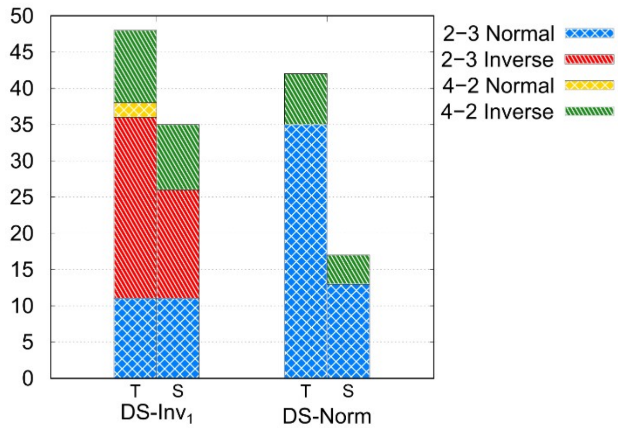

Fig. S2. Histogram showing the total number (T) and number of stable spinels (S) of different spinel type for DS-Inv$_1$ and DS-Norm double spinels. Spinel DS-Norm-3 Normal, 2-3 Inverse, 4-2 Normal and 4-2 Inverse are shown in blue, red, yellow and green, respectively. Normal and inverse type are shown in lattice and striped pattern, respectively.

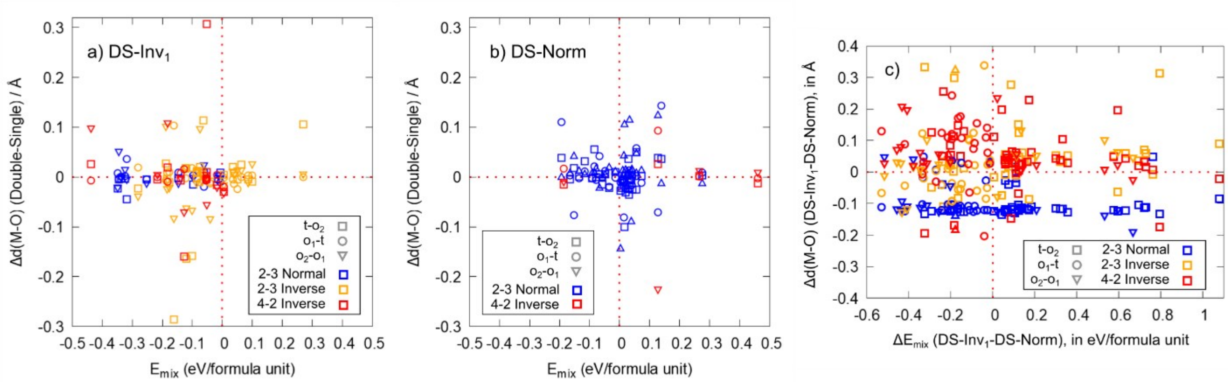

Fig. S3. Cation–oxygen distance difference (Δd(M–O)) between the double spinel and reference single spinels in: a) DS-Inv$_1$, and b) DS-Norm double spinel as a function of the E_{mix}. c) Δd(M–O) between DS-Inv$_1$ and DS-Norm double spinel as a function of the difference in E_{mix} (ΔE_{mix}) between the two types. The Δd(M–O) is calculated between the same cations in the three sites: tetrahedral (t), octahedral 1 (o_1) and 2 (o_2). The data from the 2-3 normal, 2-3 inverse and 4-2 inverse spinel is shown in blue, orange and red, respectively.

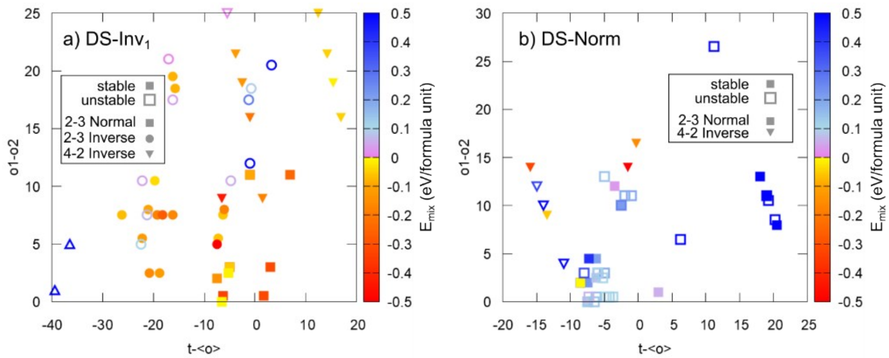

Fig. S4. Relation between tetrahedral–average octahedral site ionic radii and octahedral–octahedral ionic radii in: a) DS-Inv$_1$, and b) DS-Norm double spinels. Filled and open points show stable and unstable double spinels, respectively, respectively. The data from the 2-3 normal, 2-3 inverse and 4-2 inverse spinel is shown with square, circle and triangle points, respectively.

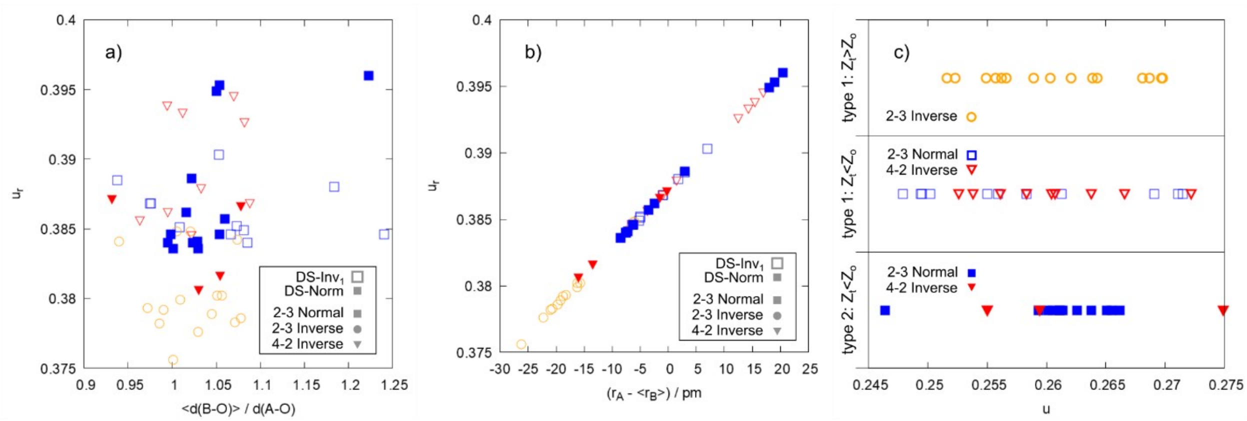

Fig. S5 Separating the double spinels based on: a) Sickafus et. al. [2], b) Yokoyama et. al. [3] and c) Stevanović et. al. [4] methods. A and B refers to the cations in a tetrahedral and octahedral site, respectively. Open and filled points show DS-Inv$_1$ and DS-Norm double spinel data, respectively. The data from the 2-3 normal, 2-3 inverse and 4-2 inverse spinel is shown with square, circle and triangle points, respectively. u_r and u are the anionic parameters, calculated using the equations: $u_r = \frac{r_A - \langle r_B \rangle}{(1+\sqrt{3})a} + \frac{1.058}{1+\sqrt{3}}$, $\langle r_B \rangle$ is the average ionic radius on octahedral site; and $u = \frac{d(M_t - O)}{a\sqrt{3}} + \frac{1}{8}$, $d(M_t$–$O)$ is the average distance between oxygen and the cation in tetrahedral site.

References:

[1] Commentary: The Materials Project: A materials genome approach to accelerating materials innovation. Jain, Anubhav, et al. s.l. : AIP Publishing, 7 2013, APL Materials, Vol. 1, p. 011002.
[2] Structure of Spinel. Sickafus, Kurt E., Wills, John M. and Grimes, Norman W. s.l. : Wiley, 12 2004, Journal of the American Ceramic Society, Vol. 82, pp. 3279–3292.
[3] Relationship between Average Cation Radii and Oxygen Parameter for Various Oxides with Spinel-Type Structure. Yokoyama, Takashi and Meguro, Takeshi. s.l. : IOP Publishing, 8 2005, Japanese Journal of Applied Physics, Vol. 44, pp. 6201–6203.
[4] Simple Point-Ion Electrostatic Model Explains the Cation Distribution in Spinel Oxides. Stevanović, Vladan, d'Avezac, Mayeul and Zunger, Alex. s.l. : American Physical Society (APS), 8 2010, Physical Review Letters, Vol. 105.