Supplementary Information for:

Synthesis of non-toxic inorganic blue pigments in the melilite-type structure

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1.) CIE *L*a*b** color coordinates

2.) Crystallographic data of Rietveld refinements

3.) Rietveld plots

Table S1: CIE $L^*a^*b^*$ color coordinates of the $Sr_2Mg_{1-x}Mn_xGe_{2-y}Si_yO_{7+\delta}$ ($0 \leq x \leq 1$; $0 \leq y \leq 2$) samples.

Sample	L^*	a^*	b^*
$Sr_2MgGe_2O_7$	92.62	0.13	-3.14
$Sr_2Mg_{0.8}Mn_{0.2}Ge_2O_{7+\delta}$	47.15	6.93	-26.24
$Sr_2Mg_{0.6}Mn_{0.4}Ge_2O_{7+\delta}$	34.90	8.39	-23.60
$Sr_2Mg_{0.4}Mn_{0.6}Ge_2O_{7+\delta}$	24.48	7.61	-17.26
$Sr_2Mg_{0.2}Mn_{0.8}Ge_2O_{7+\delta}$	25.31	4.43	-16.66
$Sr_2MnGe_2O_7$	22.77	1.71	-3.52
$Sr_2Mg_{0.8}Mn_{0.2}Ge_{1.5}Si_{0.5}O_{7+\delta}$	51.53	3.82	-23.67
$Sr_2Mg_{0.6}Mn_{0.4}Ge_{1.5}Si_{0.5}O_{7+\delta}$	33.16	7.62	-24.74
$Sr_2Mg_{0.2}Mn_{0.8}Ge_{1.5}Si_{0.5}O_{7+\delta}$	29.01	6.40	-17.60
$Sr_2Mg_{0.8}Mn_{0.2}GeSiO_{7+\delta}$	62.52	2.79	-22.64
$Sr_2Mg_{0.6}Mn_{0.4}GeSiO_{7+\delta}$	29.98	8.82	-25.07
$Sr_2Mg_{0.3}Mn_{0.7}GeSiO_{7+\delta}$	27.52	7.39	-17.89
$Sr_2Mg_{0.2}Mn_{0.8}GeSiO_{7+\delta}$	27.60	8.89	-22.11
$Sr_2Mg_{0.8}Mn_{0.2}Ge_{0.5}Si_{1.5}O_{7+\delta}$	64.48	2.12	-19.96
$Sr_2Mg_{0.6}Mn_{0.4}Ge_{0.5}Si_{1.5}O_{7+\delta}$	35.56	8.03	-26.70
$Sr_2Mg_{0.2}Mn_{0.8}Ge_{0.5}Si_{1.5}O_{7+\delta}$	31.43	10.79	-27.76
$Sr_2MnGe_{0.5}Si_{1.5}O_{7+\delta}$	28.31	10.57	-25.61
$Sr_2Mg_{0.8}Mn_{0.2}Ge_{0.4}Si_{1.6}O_{7+\delta}$	57.43	4.32	-24.25
$Sr_2Mg_{0.6}Mn_{0.4}Ge_{0.4}Si_{1.6}O_{7+\delta}$	47.80	7.14	-27.31
$Sr_2Mg_{0.2}Mn_{0.8}Ge_{0.4}Si_{1.6}O_{7+\delta}$	33.03	9.93	-27.05
$Sr_2Mg_{0.1}Mn_{0.9}Ge_{0.4}Si_{1.6}O_{7+\delta}$	31.43	9.78	-25.72
$Sr_2MnGe_{0.4}Si_{1.6}O_{7+\delta}$	28.53	9.26	-23.24

$Sr_2Mg_{0.3}Mn_{0.7}Ge_{0.3}Si_{1.7}O_{7+\delta}$	36.43	10.31	-29.55
$Sr_2Mg_{0.2}Mn_{0.8}Ge_{0.3}Si_{1.7}O_{7+\delta}$	33.04	10.54	-28.53
$Sr_2Mg_{0.8}Mn_{0.2}Ge_{0.2}Si_{1.8}O_{7+\delta}$	66.74	2.66	-21.03
$Sr_2Mg_{0.5}Mn_{0.5}Ge_{0.2}Si_{1.8}O_{7+\delta}$	45.98	7.45	-28.76
$Sr_2Mg_{0.3}Mn_{0.7}Ge_{0.2}Si_{1.8}O_{7+\delta}$	37.85	10.10	-30.71
$Sr_2Mg_{0.2}Mn_{0.8}Ge_{0.2}Si_{1.8}O_{7+\delta}$	35.67	10.92	-31.16
$Sr_2MnGe_{0.5}Si_{1.8}O_{7+\delta}$	32.15	10.51	-29.19
$Sr_2Mg_{0.2}Mn_{0.8}Ge_{0.1}Si_{1.9}O_{7+\delta}$	30.44	10.47	-28.05
$Sr_2Mg_{0.1}Mn_{0.9}Ge_{0.1}Si_{1.9}O_{7+\delta}$	35.47	10.57	-31.06
$Sr_2MnGe_{0.1}Si_{1.9}O_{7+\delta}$	32.30	11.17	-29.87
$Sr_2Mg_{0.8}Mn_{0.2}Ge_{0.05}Si_{1.95}O_{7+\delta}$	79.22	1.36	-13.18
$Sr_2Mg_{0.5}Mn_{0.5}Ge_{0.05}Si_{1.95}O_{7+\delta}$	53.08	5.20	-26.29
$Sr_2Mg_{0.2}Mn_{0.8}Ge_{0.05}Si_{1.95}O_{7+\delta}$	47.70	5.68	-28.55
$Sr_2MnGe_{0.05}Si_{1.95}O_{7+\delta}$	38.93	8.98	-30.97
$Sr_2MgSi_2O_7$	2.97	4.97	1.97
$Sr_2Mg_{0.8}Mn_{0.2}Si_2O_{7+\delta}$	77.39	1.46	-25.46
$Sr_2Mg_{0.6}Mn_{0.4}Si_2O_{7+\delta}$	57.88	5.01	-27.04
$Sr_2Mg_{0.5}Mn_{0.5}Si_2O_{7+\delta}$	57.18	5.08	-28.53
$Sr_2Mg_{0.4}Mn_{0.6}Si_2O_{7+\delta}$	49.08	7.27	-30.05
$Sr_2Mg_{0.3}Mn_{0.7}Si_2O_{7+\delta}$	43.33	8.07	-31.27
$Sr_2Mg_{0.2}Mn_{0.8}Si_2O_{7+\delta}$	45.11	7.35	-31.35
$Sr_2MnSi_2O_7$	43.53	6.19	-29.62
$CoAl_2O_4$ (Cobalt blue PB28)	39.41	3.76	-46.01

Table S2: Crystallographic data of the Rietveld refinements.

Sample	$Sr_2Mg_{0.2}Mn_{0.8}Si_2O_{7+\delta}$	$Sr_2Mg_{0.2}Mn_{0.8}Ge_{0.5}Si_{1.5}O_{7+\delta}$	$Sr_2Mg_{0.2}Mn_{0.8}GeSiO_{7+\delta}$
Crystal system	tetragonal		
Space group	P**Error!**2_1m		
a /Å	8.0925(3)	8.0553(4)	8.07216(3)
c /Å	5.1534(3)	5.2275(5)	5.2866(4)
V /Å^3	337.49(3)	339.20(5)	344.51(4)
Formula units /Z	2		
GOF (χ^2)	2.71	2.63	3.06
R_{exp}	0.61	0.84	0.66
R_{wp}	1.66	2.20	2.03
R_p	1.01	1.25	1.14
Radiation	Mo-$K_{\alpha1}$ (λ = 0.7093 Å)		
Profile range /°	$1.0 \leq \theta \leq 20.2$		
Peak Type	PV-TCHZ		
Data Points	2560		
Background	Chebychev polynomial (12 parameters)		

Sample	$Sr_2Mg_{0.2}Mn_{0.8}Ge_{1.5}Si_{0.5}O_{7+\delta}$	$Sr_2MgSi_2O_{7+\delta}$	$Sr_2MnSi_2O_{7+\delta}$	$Sr_2Mg_{0.2}Mn_{0.8}Ge_2O_{7+\delta}$
Crystal system	tetragonal			
Space group	P**Error!**2_1m			
a /Å	8.0760(3)	8.0102(5)	8.0979(2)	8.0869(3)
c /Å	5.3348(3)	5.1640(5)	5.1526(3)	5.3777(4)
V /Å^3	347.95(3)	331.34(5)	337.89(3)	351.69(4)
Formula units /Z	2			
GOF (χ^2)	2.82	4.51	2.37	2.58
R_{exp}	0.59	0.39	0.63	0.73
R_{wp}	1.67	1.76	1.48	1.89
R_p	1.04	1.04	0.91	1.22
Radiation	Mo-$K_{\alpha1}$ (λ = 0.7093 Å)			
Profile range /°	$1.0 \leq \theta \leq 20.2$			
Peak Type	PV-TCHZ			
Data Points	2560			
Background	Chebychev polynomial (12 parameters)			

Sample	$Sr_2Mg_{0.8}Mn_{0.2}Si_2O_{7+\delta}$	$Sr_2Mg_{0.6}Mn_{0.4}Si_2O_{7+\delta}$	$Sr_2Mg_{0.4}Mn_{0.6}Si_2O_{7+\delta}$
Crystal system	tetragonal		
Space group	P**Error!**2_1m		
a /Å	8.0483(6)	8.0687(4)	8.0709(3)
c /Å	5.1638(7)	5.1575(4)	5.1581(3)
V /Å^3	334.48(7)	335.78(4)	336.00(3)
Formula units /Z	2		
GOF (χ^2)	2.70	3.09	2.94
R_{exp}	0.89	0.63	0.64
R_{wp}	2.39	1.94	1.89
R_p	1.39	1.20	1.13
Radiation	Mo-$K_{\alpha1}$ (λ = 0.7093 Å)		
Profile range /°	$1.0 \leq \theta \leq 20.2$		
Peak Type	PV-TCHZ		
Data Points	2560		
Background	Chebychev polynomial (12 parameters)		

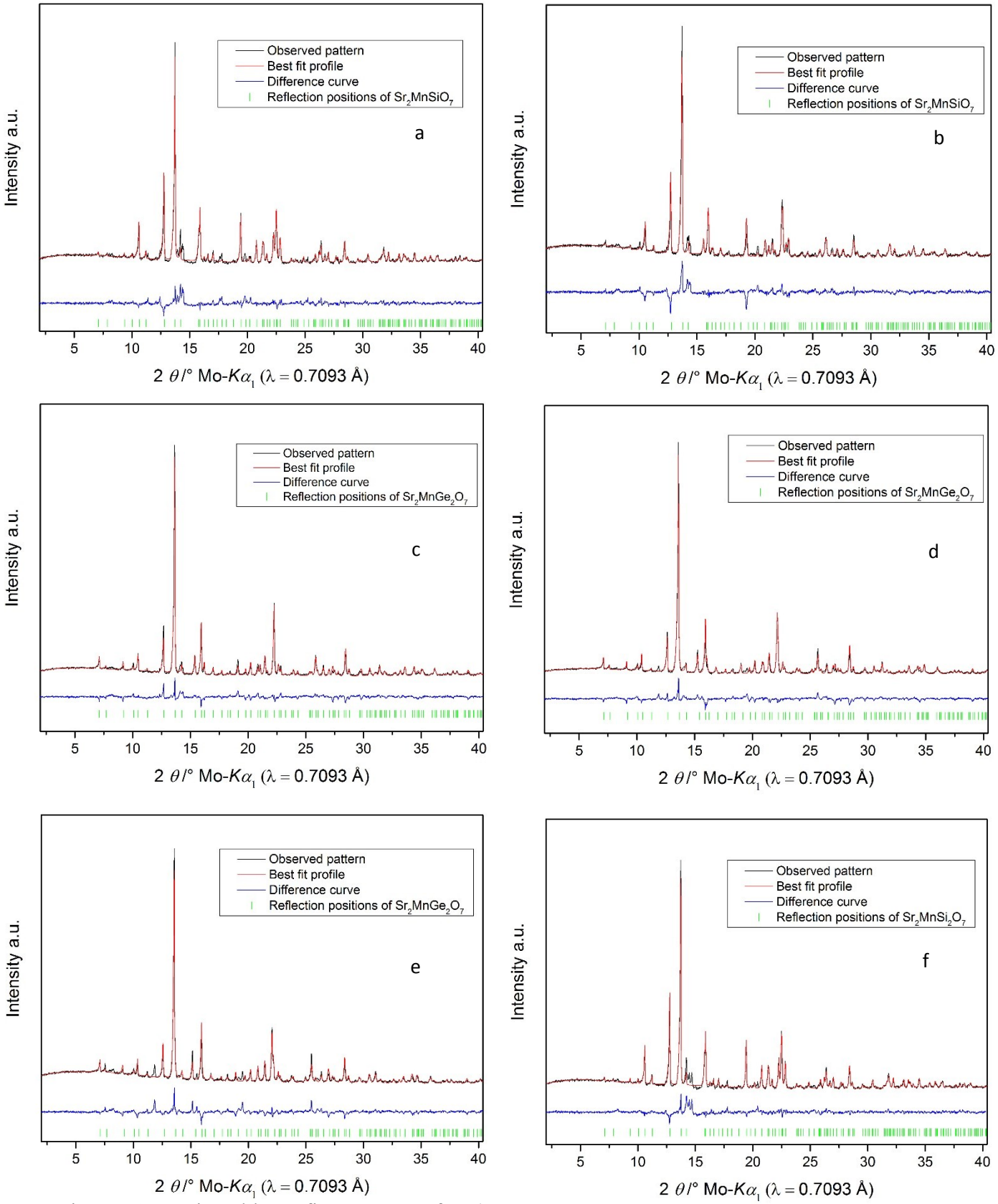

Fig. S1: Rietveld refinements of a) $Sr_2Mg_{0.2}Mn_{0.8}Si_2O_{7+\delta}$, b) $Sr_2Mg_{0.2}Mn_{0.8}Ge_{0.5}Si_{1.5}O_{7+\delta}$, c) $Sr_2Mg_{0.2}Mn_{0.8}GeSiO_{7+\delta}$, d) $Sr_2Mg_{0.2}Mn_{0.8}Ge_{1.5}Si_{0.5}O_{7+\delta}$, e) $Sr_2Mg_{0.2}Mn_{0.8}Ge_2O_{7+\delta}$, and f) $Sr_2MnSi_2O_{7+\delta}$.

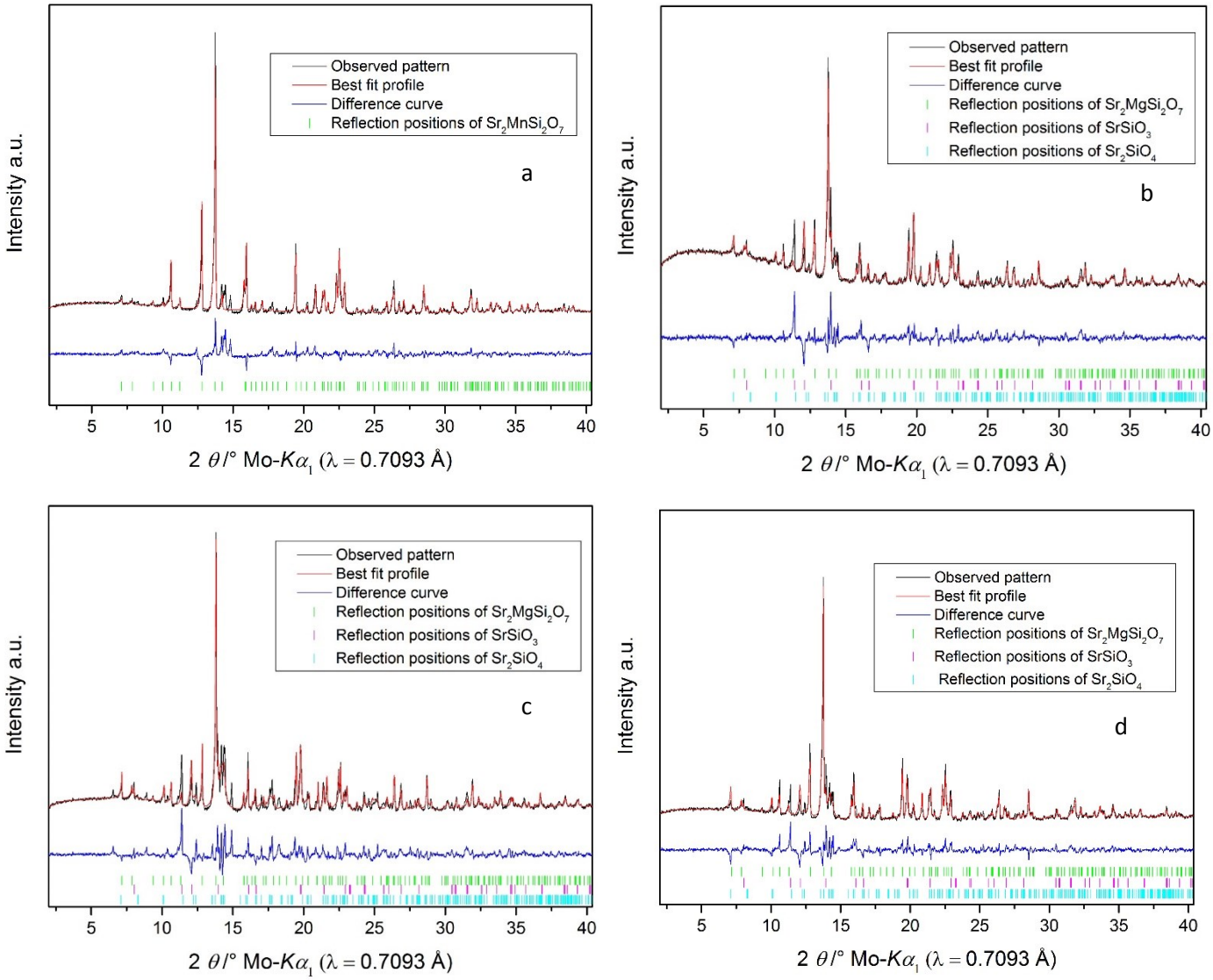

Fig. S2: Rietveld refinements of a) $Sr_2Mg_{0.4}Mn_{0.6}Si_2O_{7+\delta}$, b) $Sr_2Mg_{0.8}Mn_{0.2}Si_2O_{7+\delta}$, c) $Sr_2MgSi_2O_{7+\delta}$, and d) $Sr_2Mg_{0.6}Mn_{0.4}Si_2O_{7+\delta}$.