Electronic Supplementary Information

Design of perovskite-type fluorides cathodes for Na-ion batteries: correlation between structure and transport

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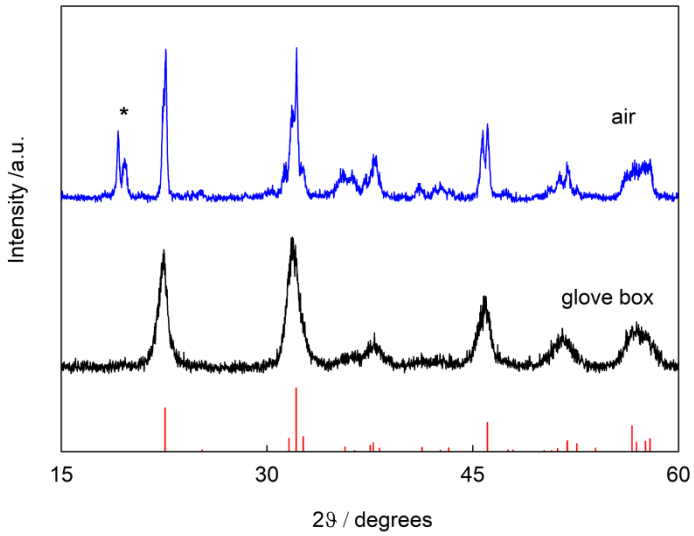

Figure S1 XRPD patterns of the $NaFeF_3$ composition (ICDD: 43-0705) prepared in air (upper part) and in Ar-filled glove box (lower part), showing the formation of impurities for the synthesis conducted in air (marked with an asterisk is the main diffraction peak of the Na_3FeF_6 phase).

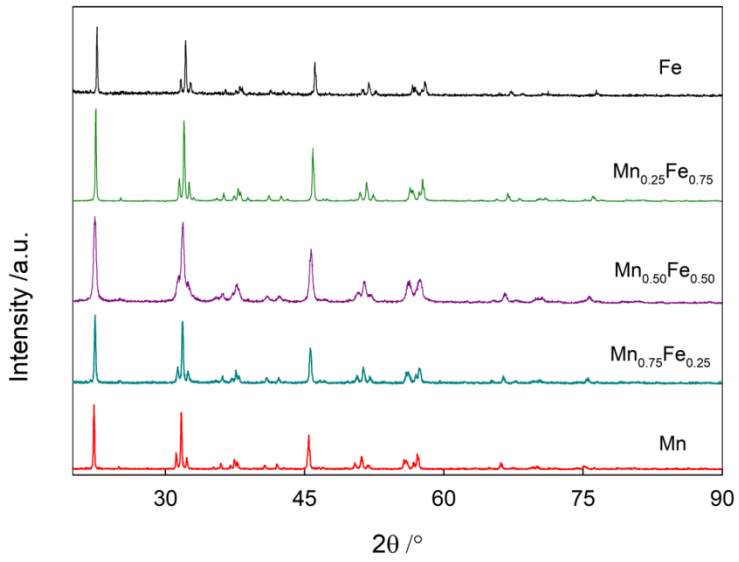

Figure S2 XRPD patterns of the $NaMn_{1-x}Fe_xF_3$ series prepared without sodium citrate, showing the formation of a solid solution over the entire compositional range.

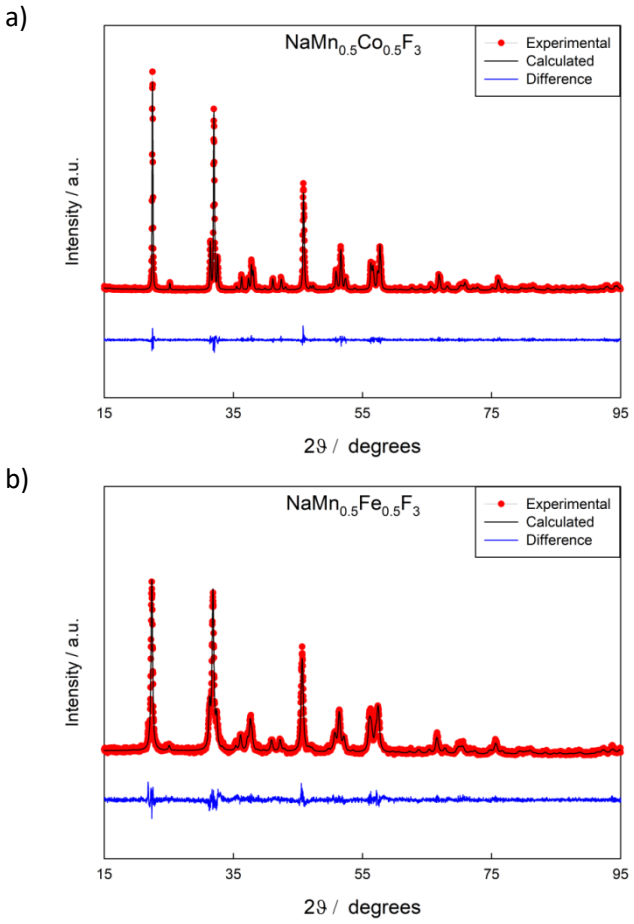

Figure S3 Rietveld refined XRPD patterns of the $NaMn_{0.5}Fe_{0.5}F_3$ and the $NaMn_{0.5}Co_{0.5}F_3$ compounds prepared without sodium citrate, showing the good agreement between experimental and calculated profiles ($\chi^2 = 1.20$; $\chi^2 = 1.43$).

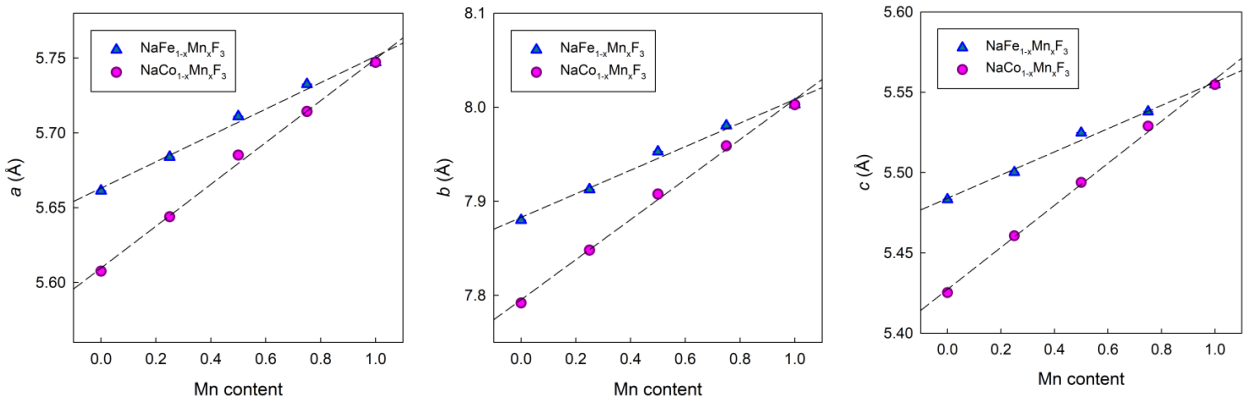

Figure S4 Lattice parameters vs composition trend for the two series, *i.e.* $NaFe_{1-x}Mn_xF_3$ and $NaCo_{1-x}Mn_xF_3$. Lines are linearly fit to the data and error bars are within the size of the symbol.

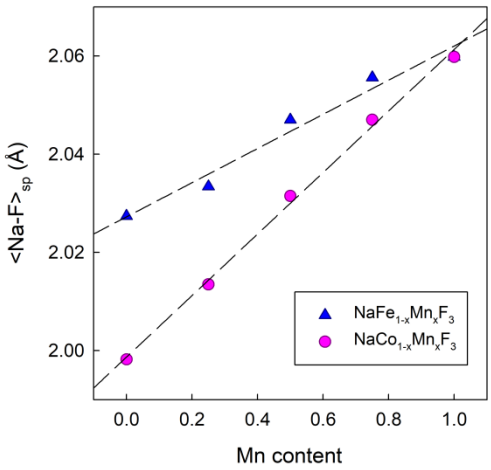

Figure S5 Average Na-F distance at the saddle point configuration as a function of the Mn content for the two series, *i.e.* $NaFe_{1-x}Mn_xF_3$ and $NaCo_{1-x}Mn_xF_3$. Lines are linearly fit to the data and error bars are within the size of the symbol.

Table S1 – Rietveld refined structural parameters of $NaCoF_3$, $NaFeF_3$ and $NaMnF_3$.

Structural parameter	$NaCoF_3$	$NaFeF_3$	$NaMnF_3$
a / Å	5.6075 (2)	5.66121(2)	5.7471(2)
b / Å	7.7919(3)	7.87985(3)	8.0028(2)
c / Å	5.4253(2)	5.48324(2)	5.5547(1)
Na *x*	0.0481(9)	0.0462(7)	0.0514(3)
Na *y*	0.25	0.25	0.25
Na *z*	-0.0117(1)	-0.0071(1)	-0.0109(3)
M *x*	0.5	0.5	0.5
M *y*	0.5	0.5	0.5
M *z*	0	0	0
F1 *x*	0.464(1)	0.455(1)	0.449(3)
F1 *y*	0.25	0.25	0.25
F1 *z*	0.101(2)	0.103(1)	0.113(3)
F2 *x*	0.1931(1)	0.1928(7)	0.1953 (2)
F2 *y*	0.5543(8)	0.559(6)	0.5609(2)
F3 *z*	0.1975(9)	0.1892(7)	0.1908(2)

Table S2 - Pair potential (Buckingham functional) and shell model parameters.

interaction	*A* (eV)	*ρ* (Å)	*C* (eV Å^6)	*k* (eV Å^{-2})	Y (e)
Na – F	2810.326262	0.246520	0	-	0
Fe – F	5485.758281	0.226408	0	19.26	2.997
Co – F	8714.28	0.2113	0	19.26	2.997
Mn – F	3177.7991	0.247763	0	19.26	2.997
F – F	1153	0.1365	0	63.57	-2.321

Table S3 – Comparison between calculated and experimental structural parameters.

Composition	parameter	Experimental	Calculated	Difference
$NaCoF_3$	*a* / Å	5.6075	5.5883	-0.0192
	b / Å	7.7919	7.8063	0.0144
	c / Å	5.4253	5.4982	0.0729
$NaFeF_3$	*a* / Å	5.6612	5.6587	-0.0025
	b / Å	7.8798	7.8689	-0.0109
	c / Å	5.4832	5.5424	0.0592
$NaMnF_3$	*a* / Å	5.7471	5.7581	0.0110
	b / Å	8.0028	7.9703	-0.0325
	c / Å	5.5547	5.6100	0.0553