

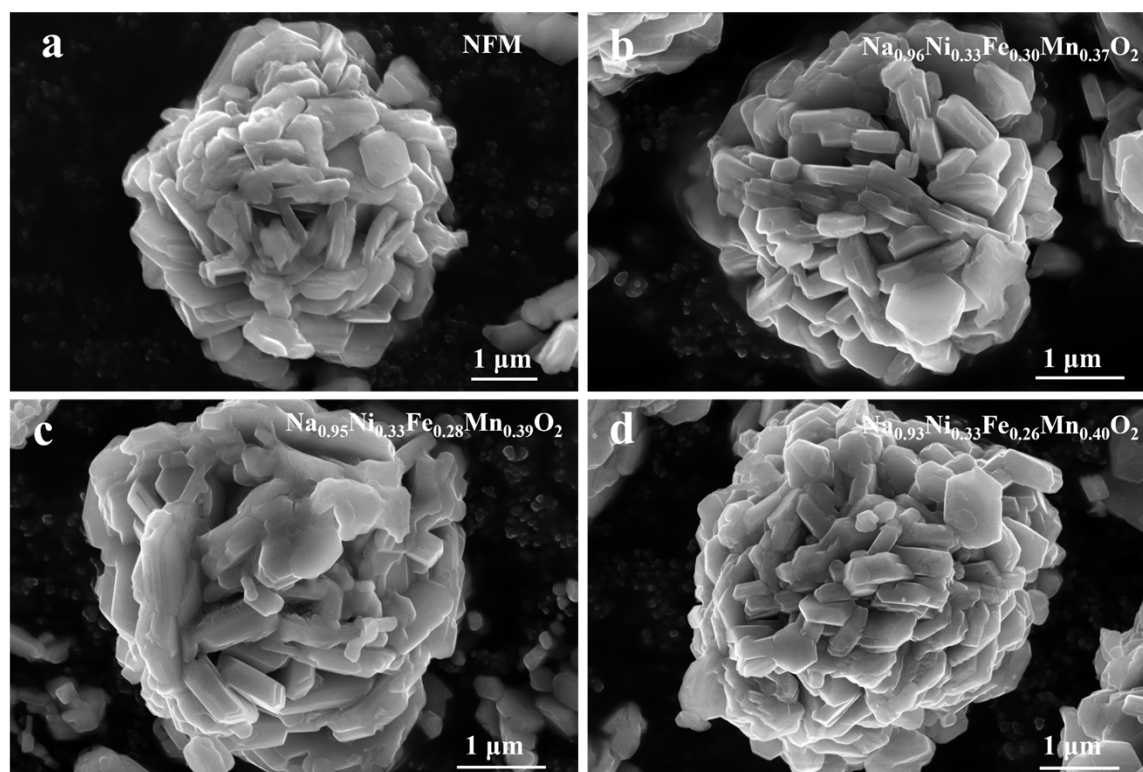


Figure S1 SEM images of NFM, $\text{Na}_{0.96}\text{Ni}_{0.33}\text{Fe}_{0.30}\text{Mn}_{0.37}\text{O}_2$, $\text{Na}_{0.95}\text{Ni}_{0.33}\text{Fe}_{0.28}\text{Mn}_{0.39}\text{O}_2$ and $\text{Na}_{0.93}\text{Ni}_{0.33}\text{Fe}_{0.26}\text{Mn}_{0.40}\text{O}_2$.

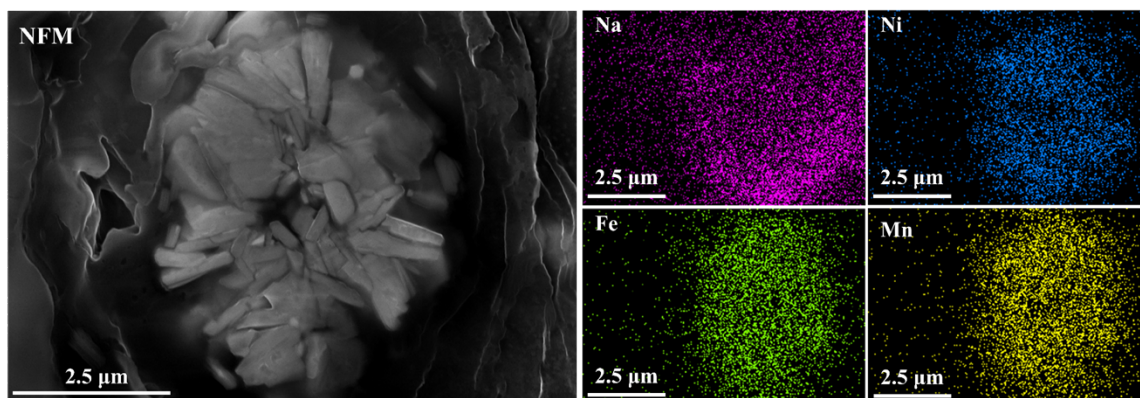


Figure S2 Cross-sectional SEM image and EDS mapping of NFM.

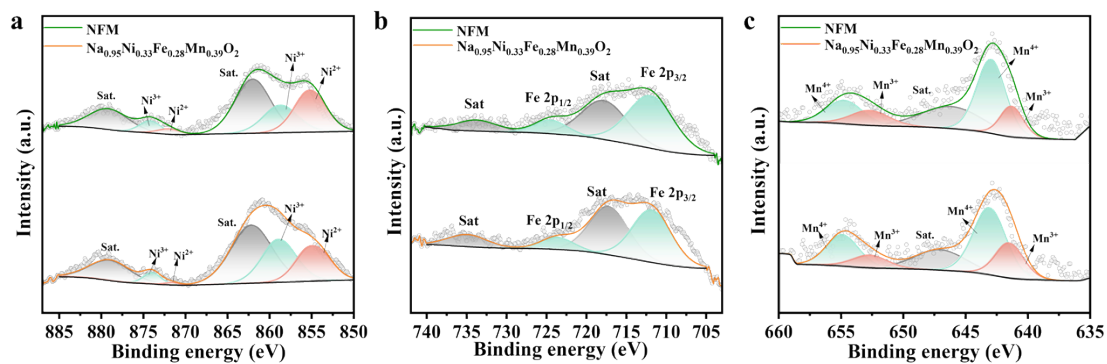


Figure S3 Ex situ XPS results of (a) Ni 2p, (b) Fe 2p and (c) Mn 2p for NFM and $\text{Na}_{0.95}\text{Ni}_{0.33}\text{Fe}_{0.28}\text{Mn}_{0.39}\text{O}_2$.

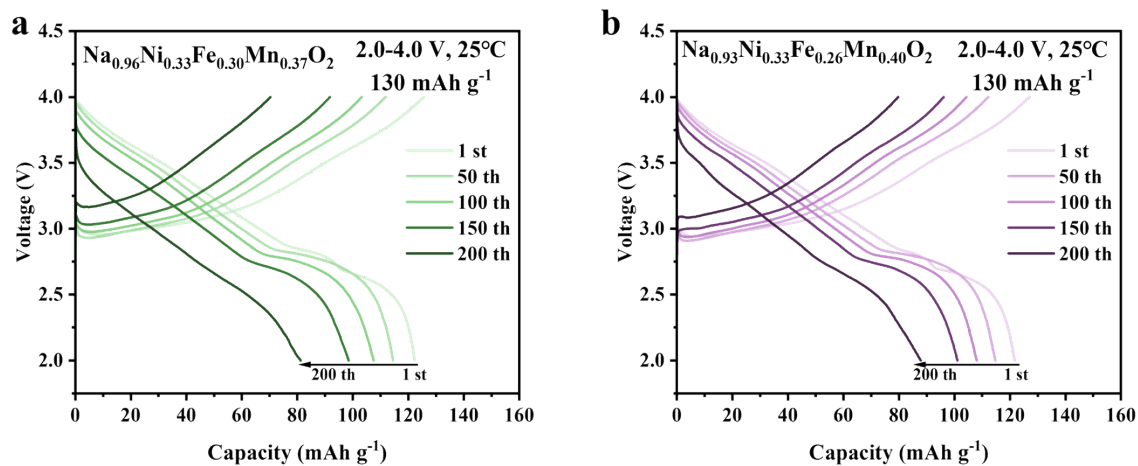


Figure S4 Charge/discharge curves of (a) $\text{Na}_{0.96}\text{Ni}_{0.33}\text{Fe}_{0.30}\text{Mn}_{0.37}\text{O}_2$ and (b) $\text{Na}_{0.93}\text{Ni}_{0.33}\text{Fe}_{0.26}\text{Mn}_{0.40}\text{O}_2$ at a rate of 1 C within the voltage range of 2.0–4.0 V.

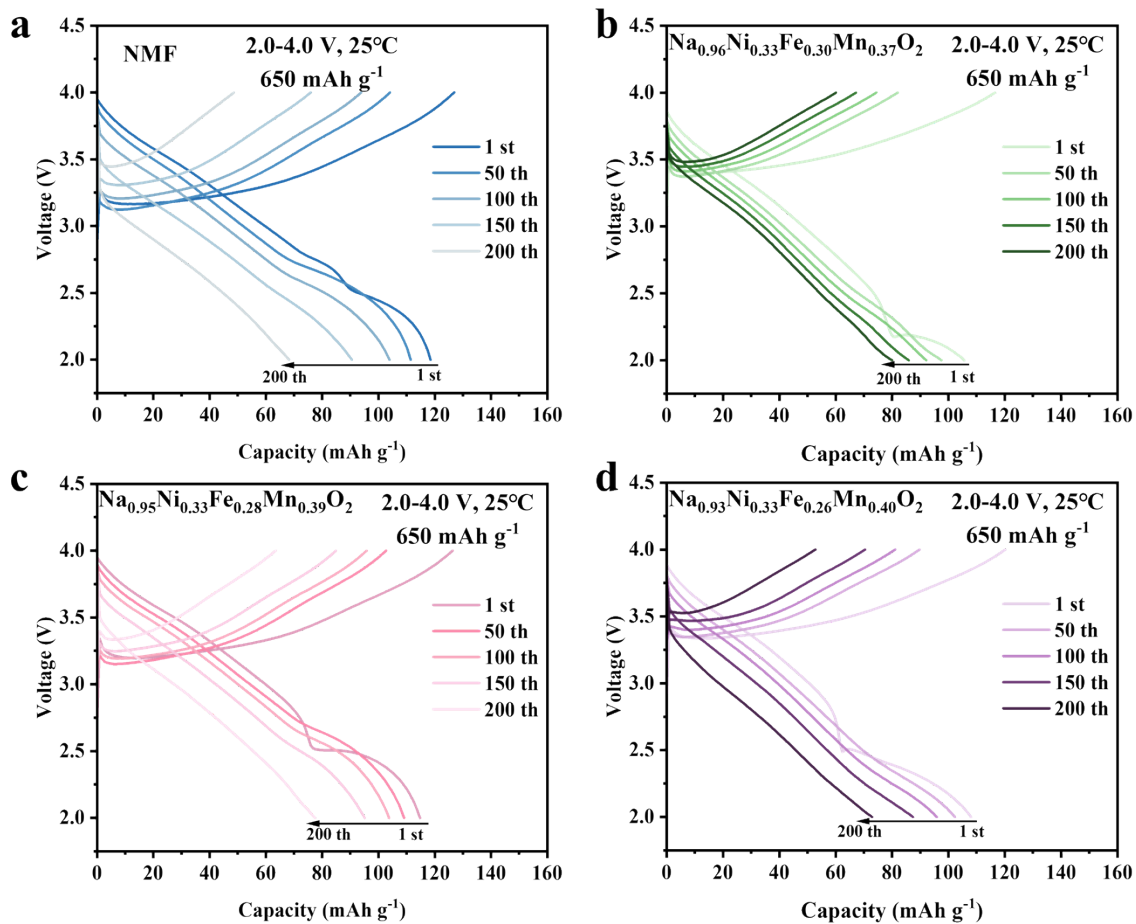


Figure S5 Charge/discharge curves of (a) NMF, (b) Na_{0.96}Ni_{0.33}Fe_{0.30}Mn_{0.37}O₂, (c) Na_{0.95}Ni_{0.33}Fe_{0.28}Mn_{0.39}O₂ and (d) Na_{0.93}Ni_{0.33}Fe_{0.26}Mn_{0.40}O₂ at a rate of 5 C within the voltage range of 2.0–4.0 V.

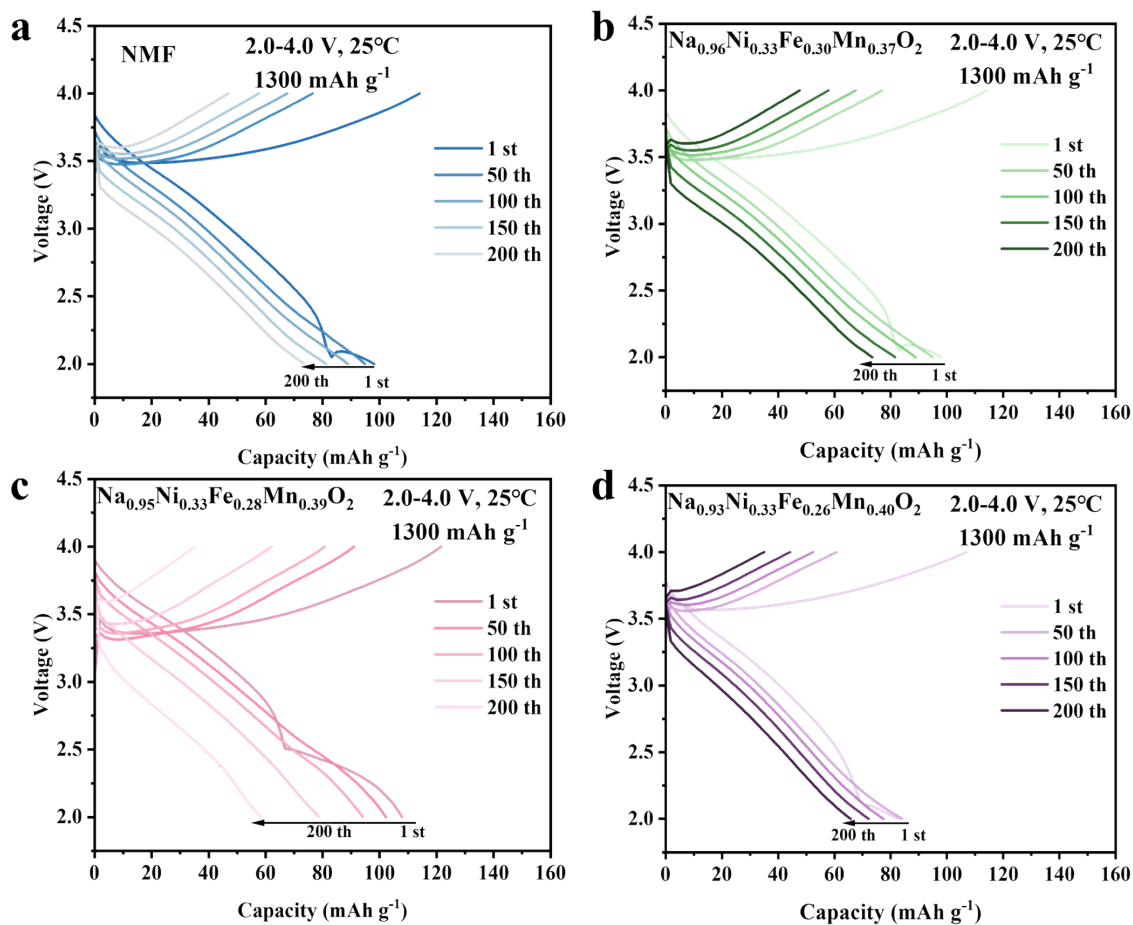


Figure S6 Charge/discharge curves of (a) NFM, (b) Na_{0.96}Ni_{0.33}Fe_{0.30}Mn_{0.37}O₂, (c) Na_{0.95}Ni_{0.33}Fe_{0.28}Mn_{0.39}O₂ and (d) Na_{0.93}Ni_{0.33}Fe_{0.26}Mn_{0.40}O₂ at a rate of 10 C within the voltage range of 2.0–4.0 V.

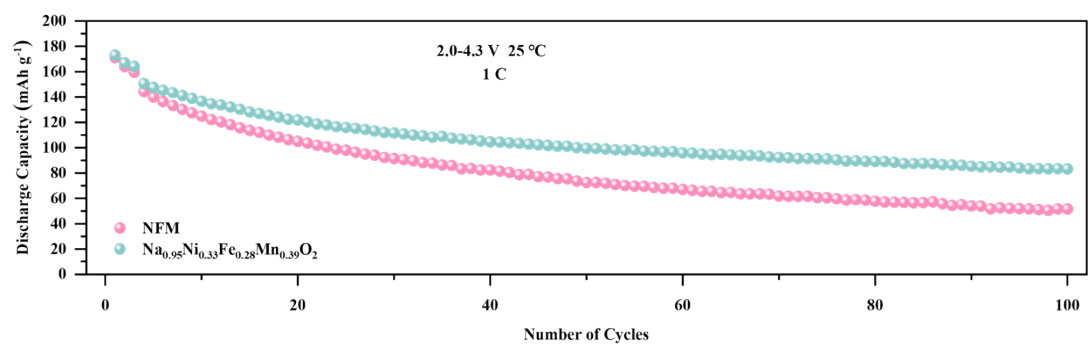


Figure S7 Long-term cycling performance of NFM and Na_{0.95}Ni_{0.33}Fe_{0.28}Mn_{0.39}O₂ at a rate of 1 C within the voltage range of 2.0–4.3 V.

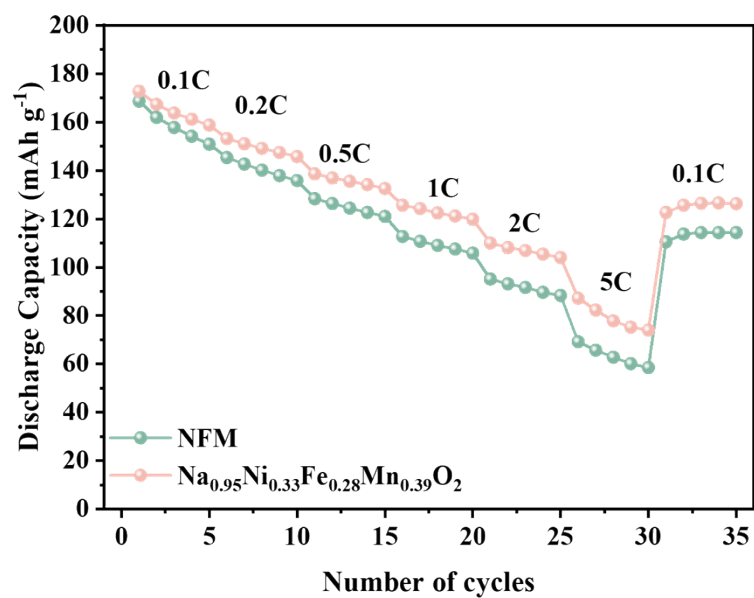


Figure S8 Rate capability of NFM and Na_{0.95}Ni_{0.33}Fe_{0.28}Mn_{0.39}O₂ within the voltage range of 2.0–4.3 V.

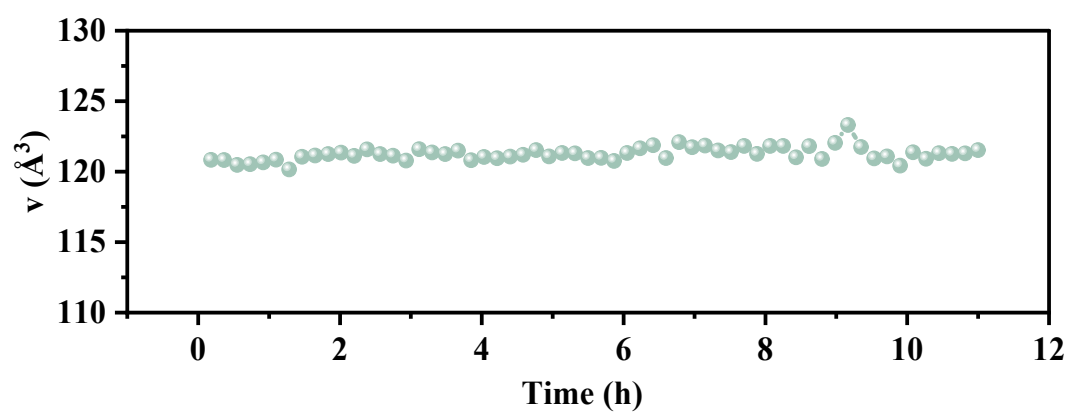


Figure S9 Volume change of $\text{Na}_{0.95}\text{Ni}_{0.33}\text{Fe}_{0.28}\text{Mn}_{0.39}\text{O}_2$ during the charge/discharge process.

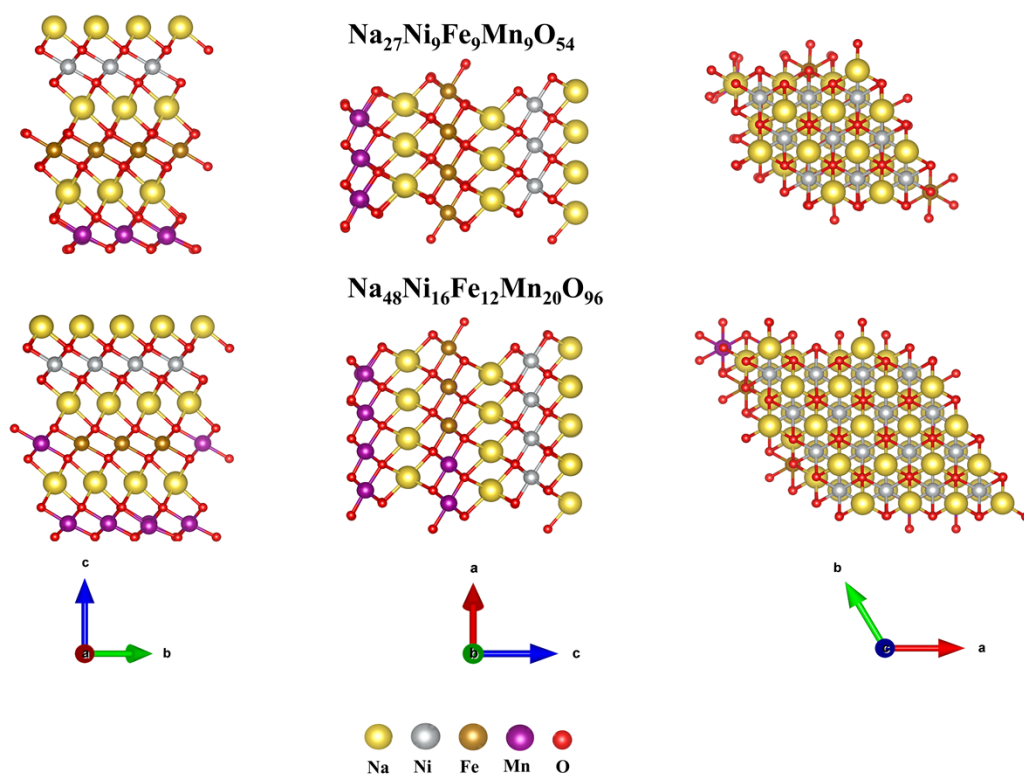


Figure S10 Optimized structural models of $\text{Na}_{27}\text{Ni}_9\text{Fe}_9\text{Mn}_9\text{O}_{54}$ and $\text{Na}_{48}\text{Ni}_{16}\text{Fe}_{12}\text{Mn}_{20}\text{O}_{96}$.

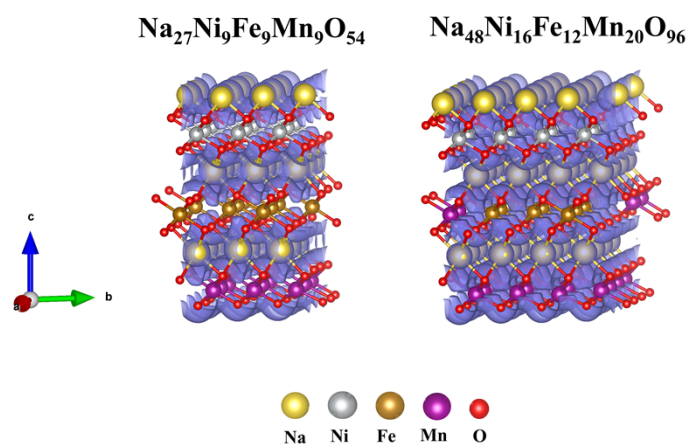


Figure S11 Three-dimensional spatial charge distribution of the structural models $\text{Na}_{27}\text{Ni}_9\text{Fe}_9\text{Mn}_9\text{O}_{54}$ and $\text{Na}_{48}\text{Ni}_{16}\text{Fe}_{12}\text{Mn}_{20}\text{O}_{96}$.

Table S1 Refinement data of all samples

Samples	a (Å)	b (Å)	c (Å)	v (Å ³)	NiO
NFM	2.979610	2.979610	16.00113	123.026876	0.003
Na _{0.96} Ni _{0.33} Fe _{0.30} Mn _{0.37} O ₂	2.968670	2.968670	16.10148	122.891401	0.026
Na _{0.95} Ni _{0.33} Fe _{0.28} Mn _{0.39} O ₂	2.965750	2.965750	16.08758	122.543632	0.024
Na _{0.93} Ni _{0.33} Fe _{0.26} Mn _{0.40} O ₂	2.963520	2.963520	16.10840	122.517226	0.025

Table S2 Structural information of all samples

Samples	Na-layer (Å)	TM-layer (Å)	Na-O (Å)	TM-O (Å)
NFM	3.18017	2.15354	2.34259	2.02948
Na _{0.96} Ni _{0.33} Fe _{0.30} Mn _{0.37} O ₂	3.19888	2.16621	2.34392	2.02703
Na _{0.95} Ni _{0.33} Fe _{0.28} Mn _{0.39} O ₂	3.19735	2.16518	3.34258	2.02581
Na _{0.93} Ni _{0.33} Fe _{0.26} Mn _{0.40} O ₂	3.20149	2.16798	2.34305	2.02546

Table S3 d-band centers of NFM

d-center	Fe	Ni	Mn	O-p
UP	-1.79372	- 2.13159	-2.86115	-3.29701
DOWN	-0.87532	-1.08928	-0.09498	-3.16720
average	-1.33452	-1.610435	-1.478065	-3.232105

Table S4 d-band centers of Na_{0.95}Ni_{0.33}Fe_{0.28}Mn_{0.39}O₂

d-center	Fe	Ni	Mn	O-p
UP	-1.27260	-1.55916	-2.70747	-3.34520
DOWN	-1.23242	-0.97174	-0.39091	-3.28297
average	-1.252510	-1.265450	-1.549190	-3.314085