Supplementary information

Aging Mechanism of Mn-based Prussian Blue Cathode Material by Synchrotron 2D X-ray Fluorescence

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Table S1. The performance of MnHCF cathode material in AZIBs.

Cathode material	Specific capacity	Capacity retention	Ref.
$K_{1.64}Mn_{1.2}Fe(CN)_6$	65.5 mAh g^{-1} at 25 mA g^{-1}	49% after 120 cycles at 200 mA g^{-1}	[1*]
$Na_2Mn[Fe(CN)_6]\cdot 2.78H_2O$	55.3 mAh g^{-1} at 50 mA g^{-1}	60% after 120 cycles at 50 mA g^{-1}	[2*]
$K_{1.76}Mn_{1.17}[Fe(CN)_6]\cdot xH_2O$	123 mAh g^{-1} at 50 mA g^{-1}	90% after 500 cycles at 250 mA g^{-1}	[29]
$K_{1.6}Mn_{1.17}[Fe(CN)_6]\cdot xH_2O$	138 mAh g^{-1} at 0.2 A g^{-1}	72.5% after 400 cycles at 0.2 A g^{-1}	[28]
$Na_{1.47}Mn[Fe(CN)_6]_{0.88}\cdot 2.6H_2O$	176 mAh g^{-1} at C/20	70% after 50 cycles at C/5	[39]
$Na_2MnFe(CN)_6$	137 mAh g^{-1} at 0.5 C	90% after 400 cycles at 0.5 C	[3*]

1* Li, Q.; Ma, K.; Yang, G.; Wang, C. High-voltage non-aqueous Zn/$K_{1.6}Mn_{1.2}Fe(CN)_6$ batteries with zero capacity loss in extremely long working duration. *Energy Storage Mater*, **2020**, *29*, 246–253. DOI: 10.1016/j.ensm.2020.04.030.

2* Li, W.; Xu, C.; Zhang, X.; Xia, M.; Yang, Z.; Yan, H.; Yu, H.; Zhang, L.; Shu, W.; Shu, J. Sodium manganese hexacyanoferrate as Zn ion host toward aqueous energy storage. *J. Electroanal. Chem.*, **2021**, *881*, 114968. DOI: 10.1016/j.jelechem.2020.114968.

3* Hou, Z.; Zhang, X.; Li, X.; Zhu, Y.; Liang, J.; Qian, Y. Surfactant widens the electrochemical window of an aqueous electrolyte for better rechargeable aqueous sodium/zinc battery. *J Mater Chem A Mater*, **2017**, *5* (2), 730–738. DOI: 10.1039/C6TA08736A.

Table S2. The list of samples analyzed with PXRD technique.

30%NiMnHCF Samples	Description
Pristine	Fresh electrode
C1	Charged after 1st cycle
D1	Discharged after 1st cycle
C2	Charged after 2nd cycle
D2	Discharged after 2nd cycle
C10	Charged after 10th cycle
D10	Discharged after 10th cycle
C50	Charged after 50th cycle
D50	Discharged after 50th cycle
C100	Charged after 100th cycle
D100	Discharged after 100th cycle

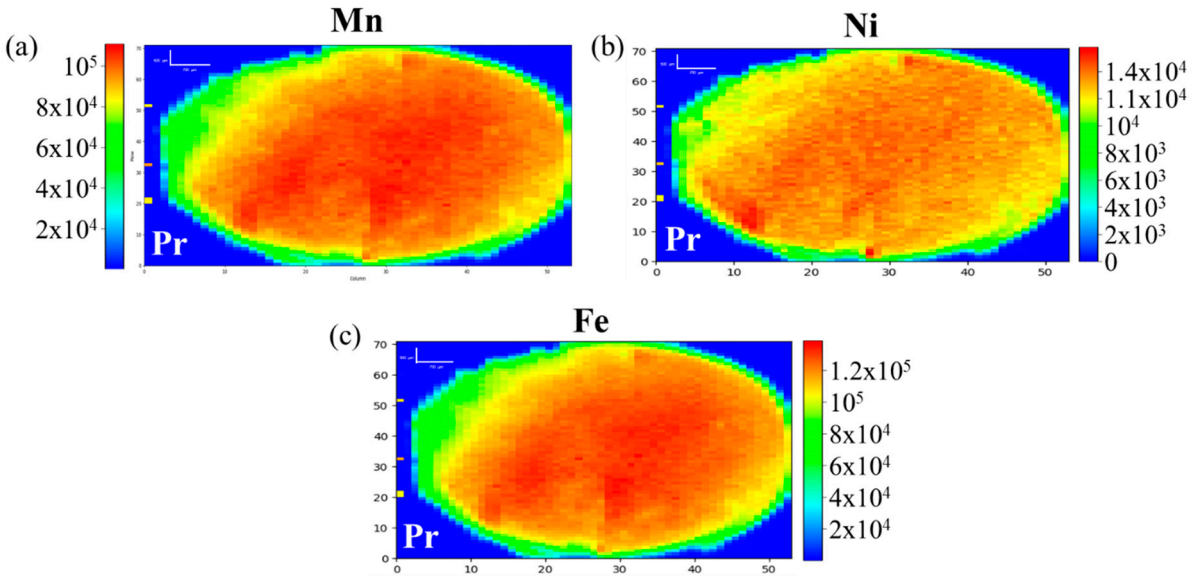

Figure S1. 2D-XRF maps of Pristine sample of 10%NiMnHCF: (a) Mn, (b) Ni and (c) Fe.

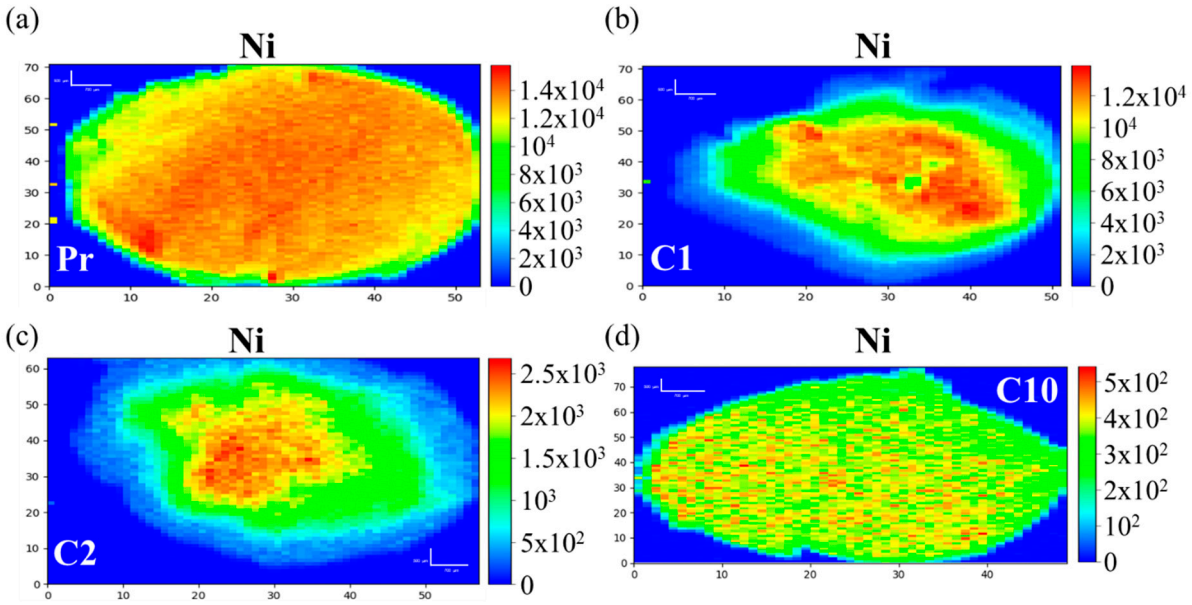

Figure S2. 2D-XRF maps of Ni contribution of 10%NiMnHCF samples: (a) Pristine, (b), C1, (c) C2 and (d) C10.

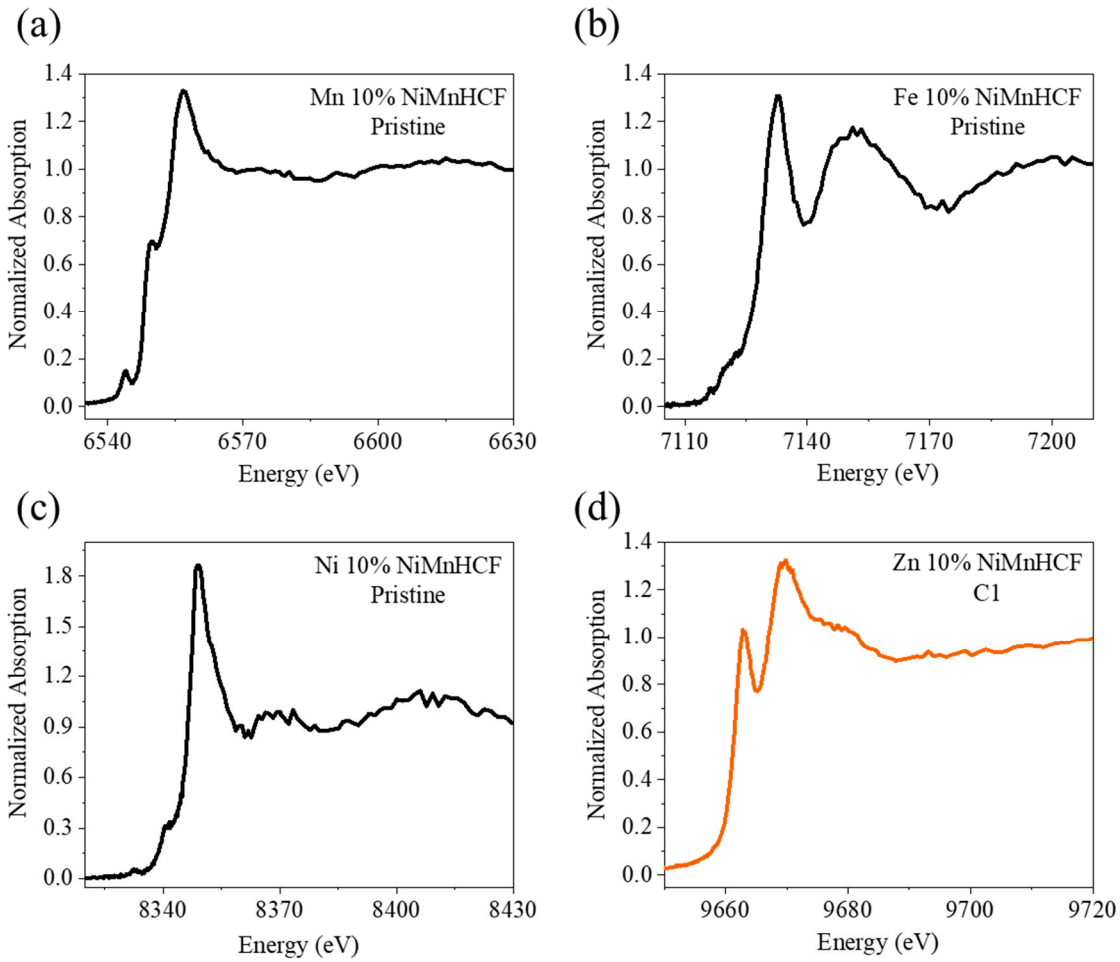

Figure S3. XANES of 10%NiMnHCF samples: (a) Mn K-edge of Pristine, (b), Fe K-edge of Pristine, (c) Ni K-edge of Pristine and (d) Zn K-edge of C1.

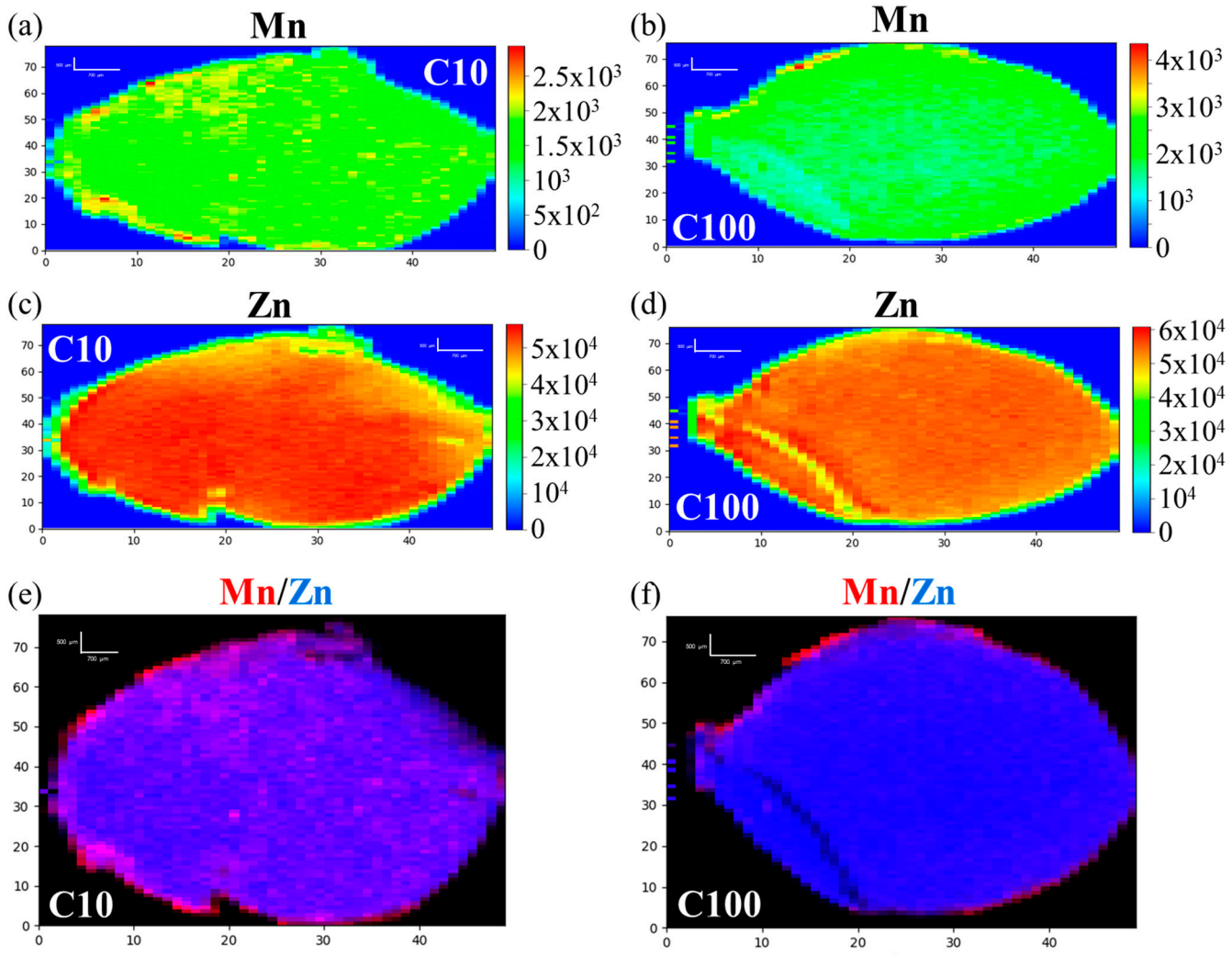

Figure S4. 2D-XRF maps of 10%NiMnHCF samples: (a) C10 Mn, (b), C100 Mn, (c) C10 Zn, (d) C100 Zn, (e) C10 Mn/Zn overlay and (f) C100 Mn/Zn overlay.

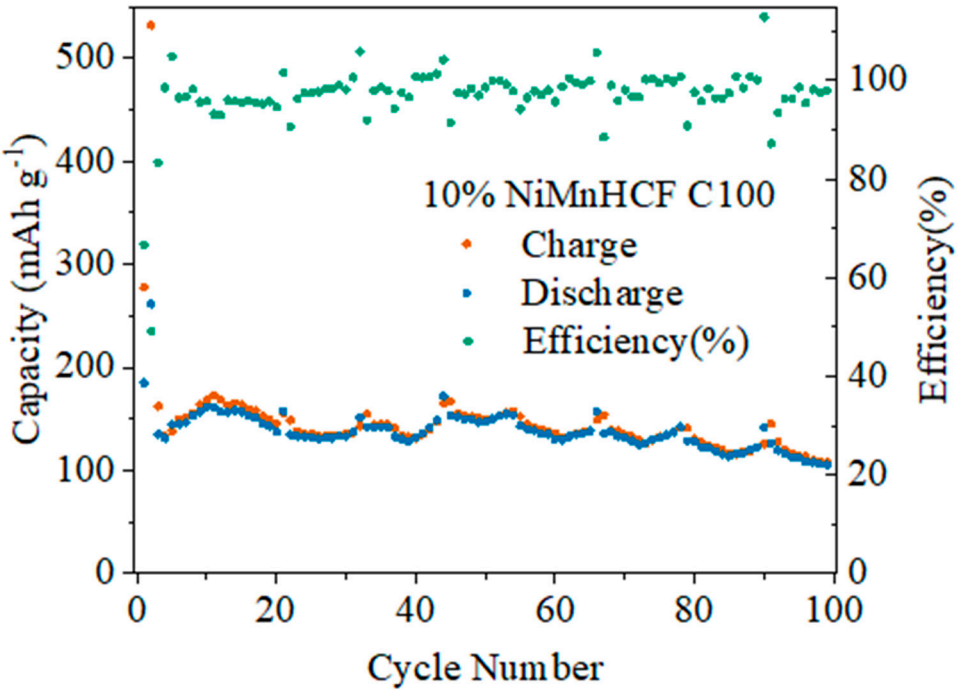

Figure S5. GCPL data of C100 of 10%NiMnHCF: stability and efficiency test.

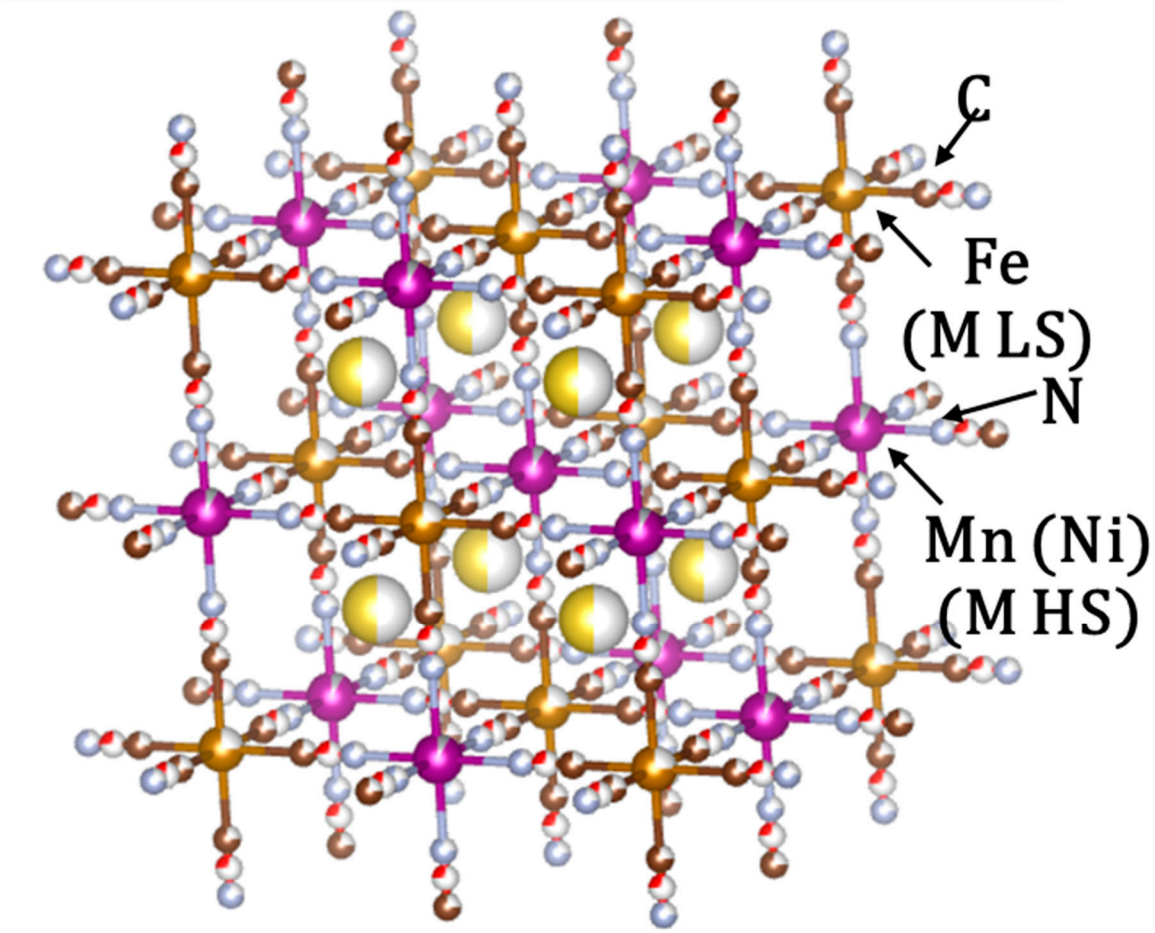

Figure S6. F m-3m structure of 30%NiMnHCF.

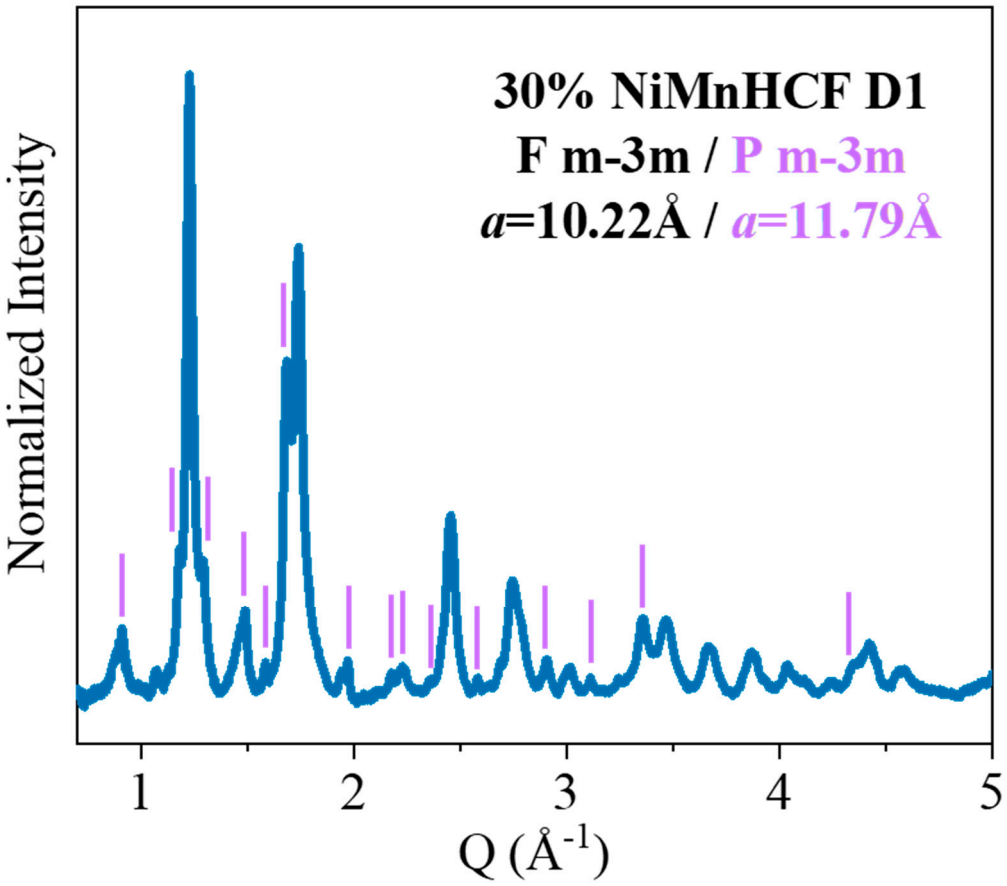

Figure S7. PXRD measurement result of D1 of 30%NiMnHCF.

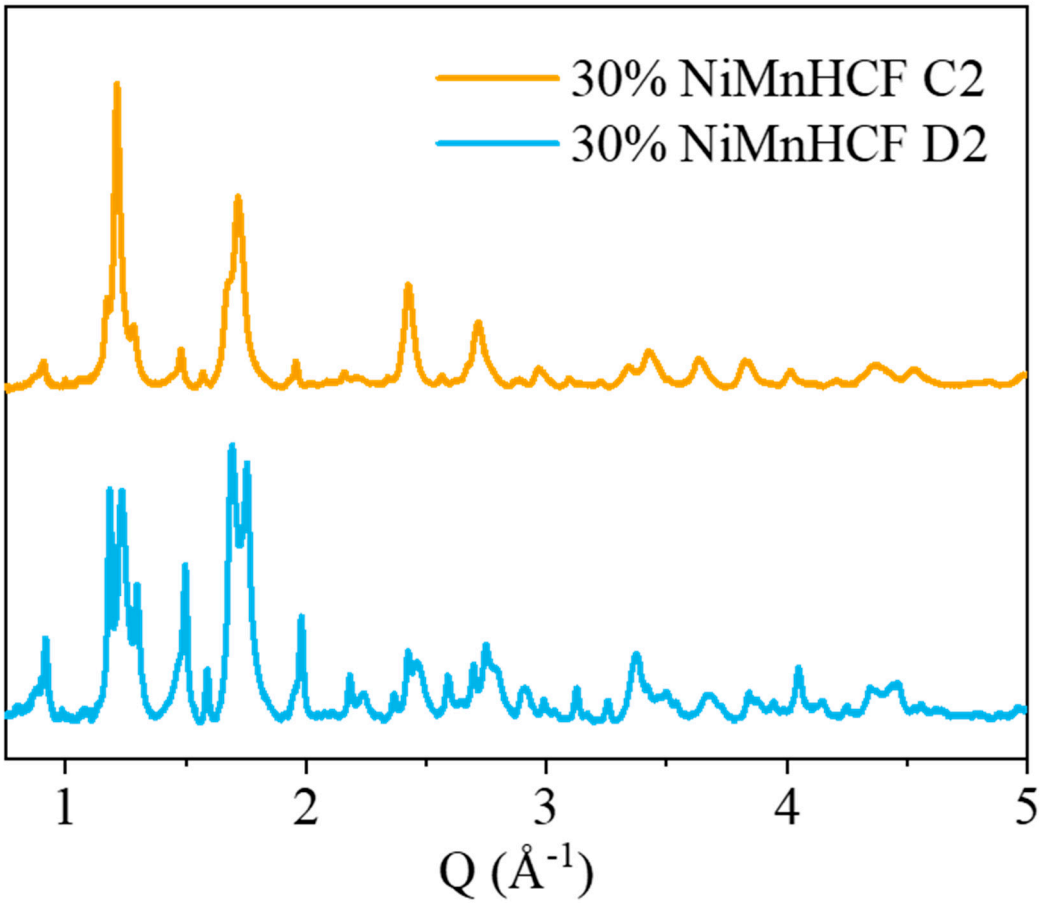

Figure S8. PXRD measurement results of C2 and D2 of 30%NiMnHCF.

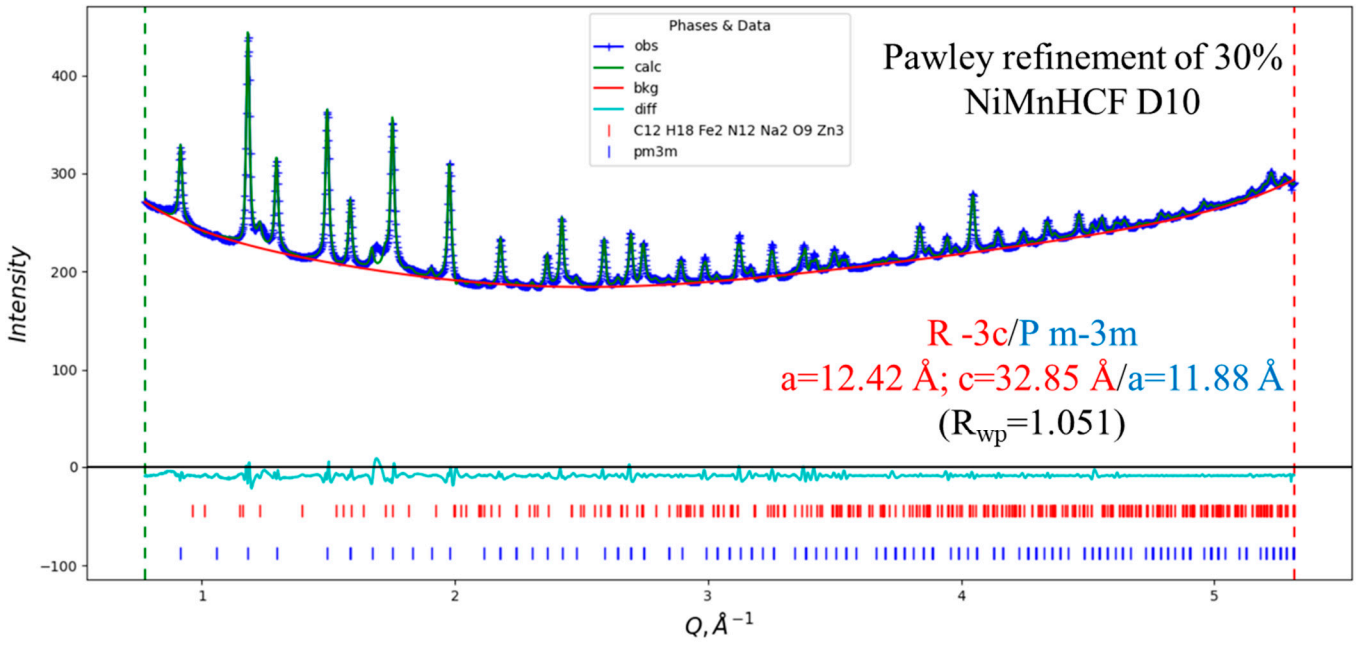

Figure S9. Pawley refinement of D10 of 30%NiMnHCF.

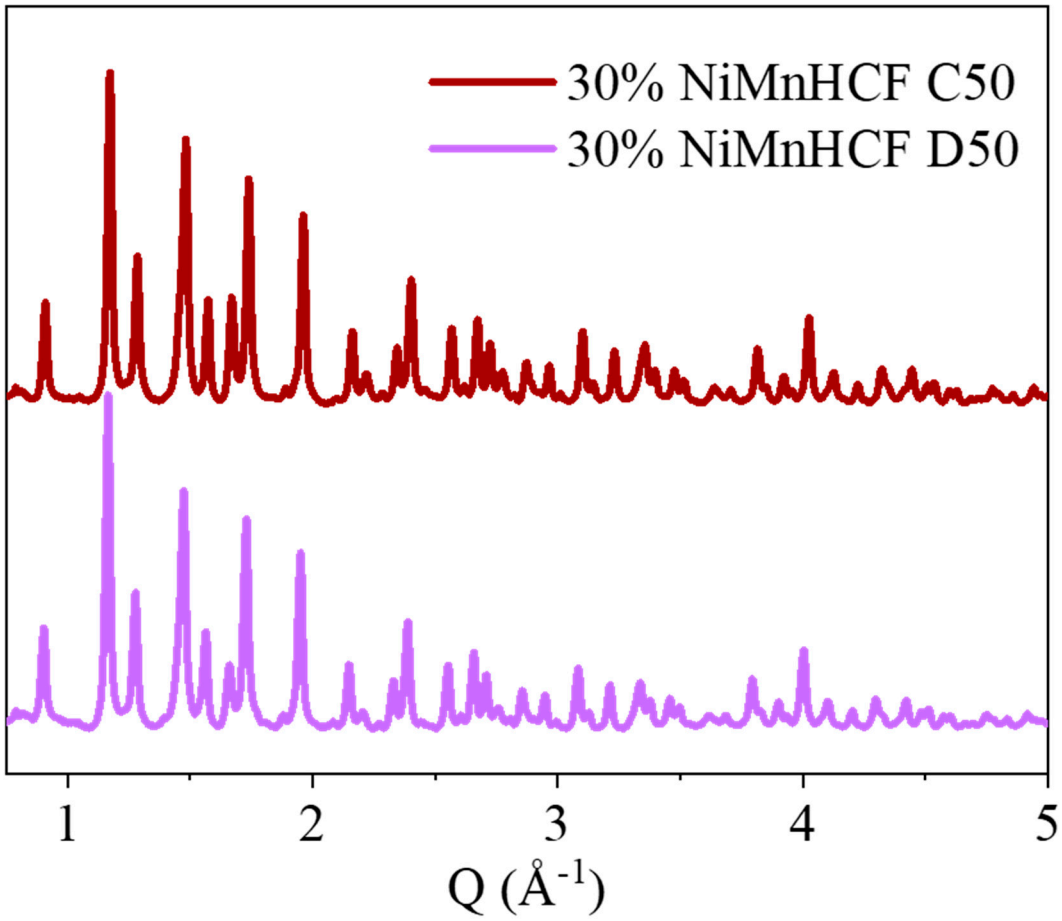

Figure S10. PXRD measurement results of C50 and D50 of 30%NiMnHCF.

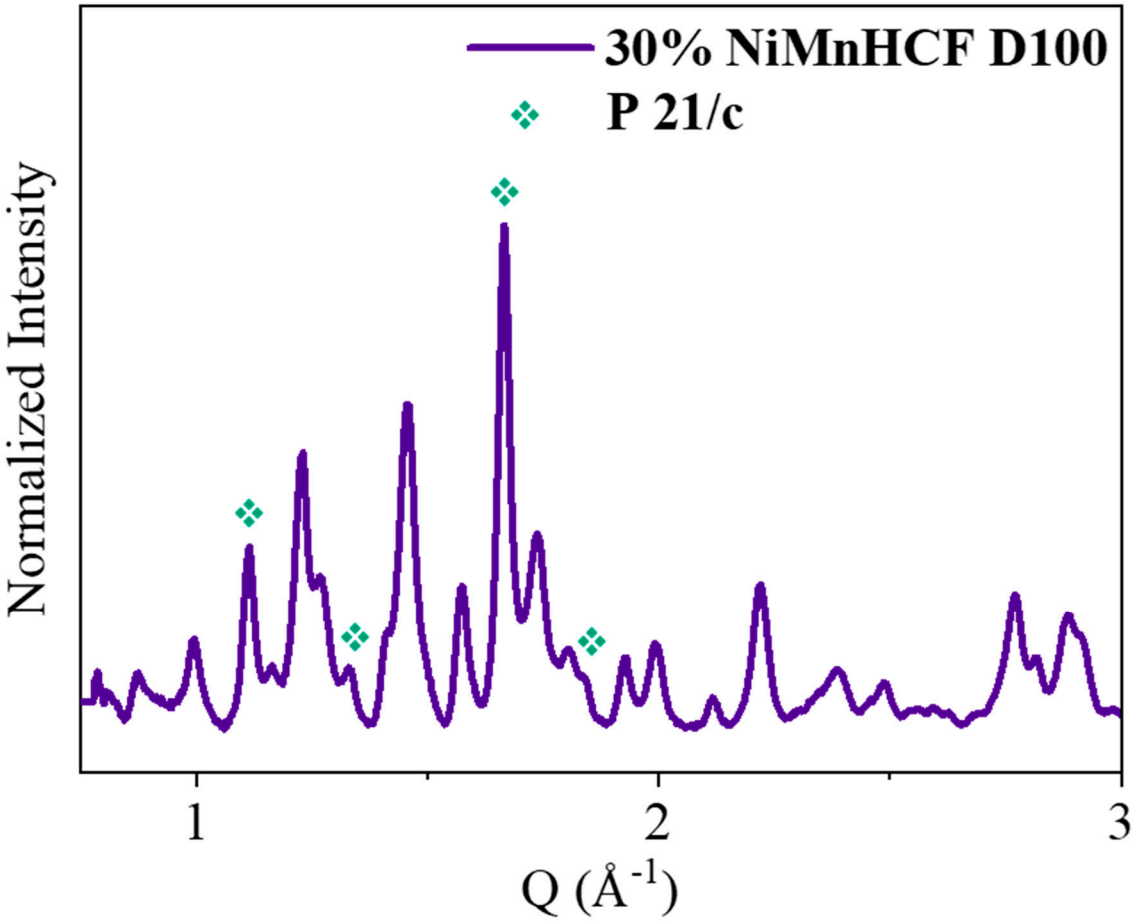

Figure S11. PXRD measurement result of D100 of 30%NiMnHCF.

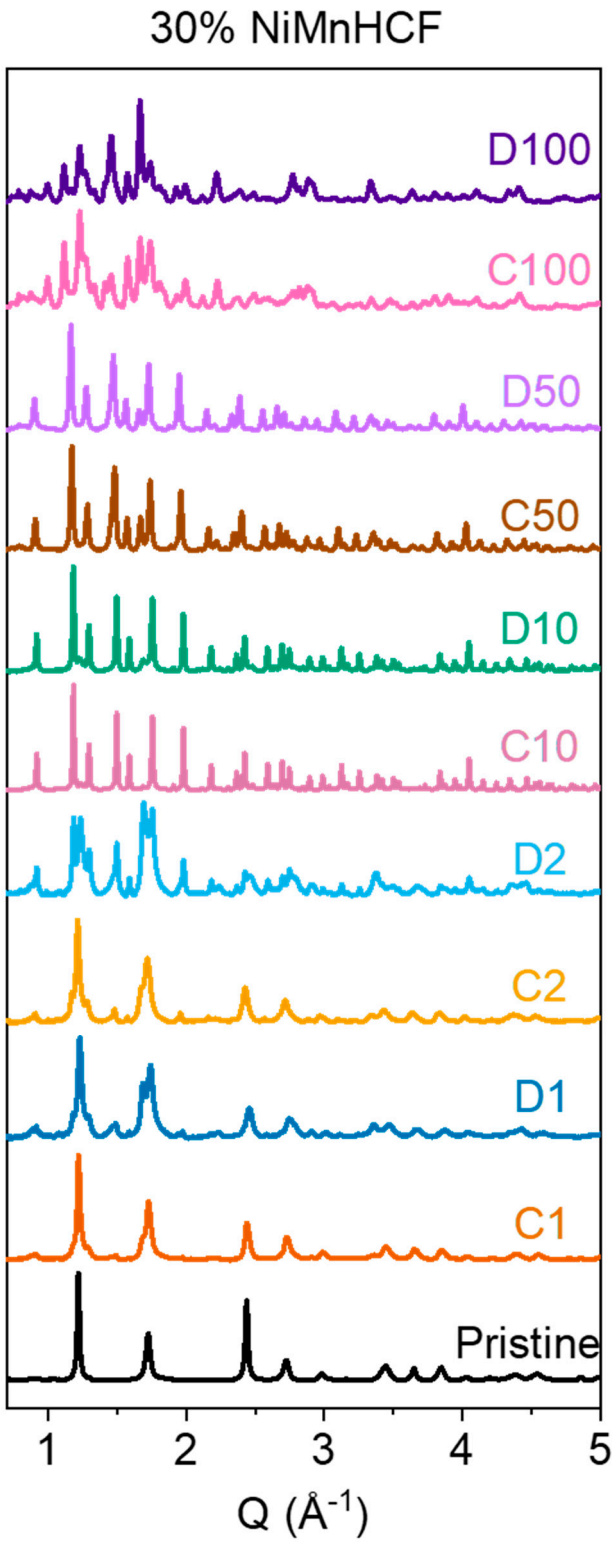

Figure S12. PXRD measurement result of D100 of 30%NiMnHCF.

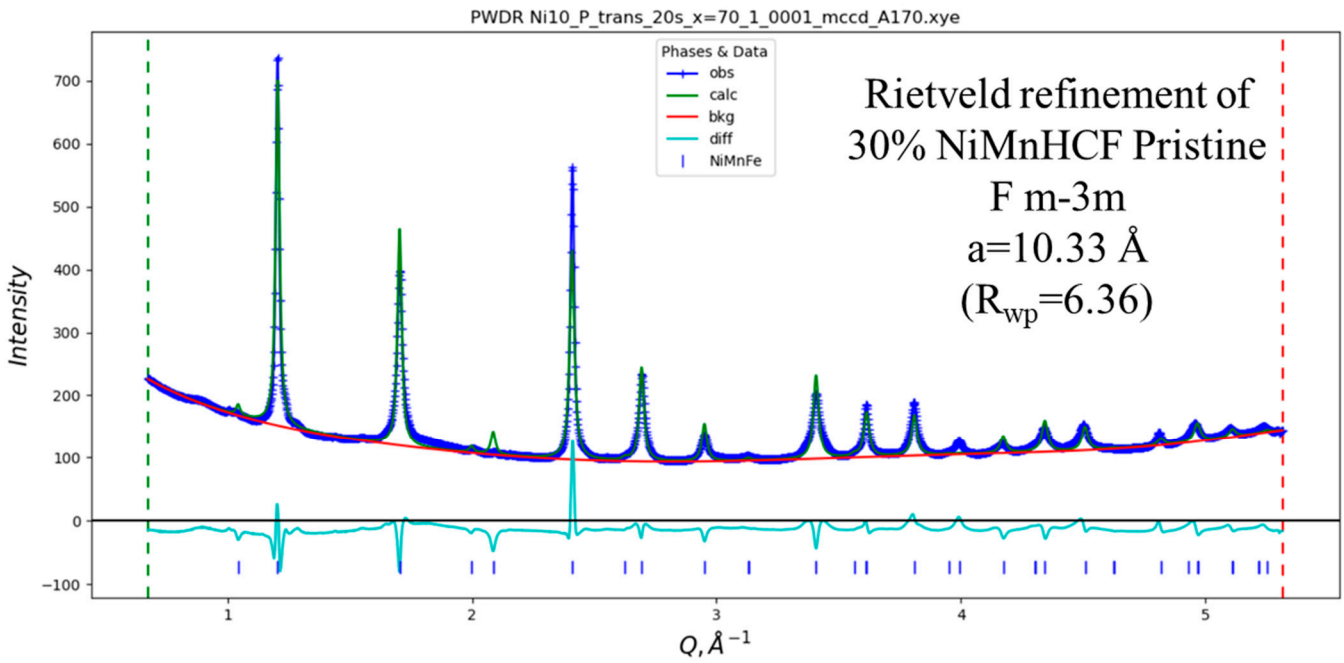

Figure S13. Rietveld refinement of Pristine of 30%NiMnHCF.

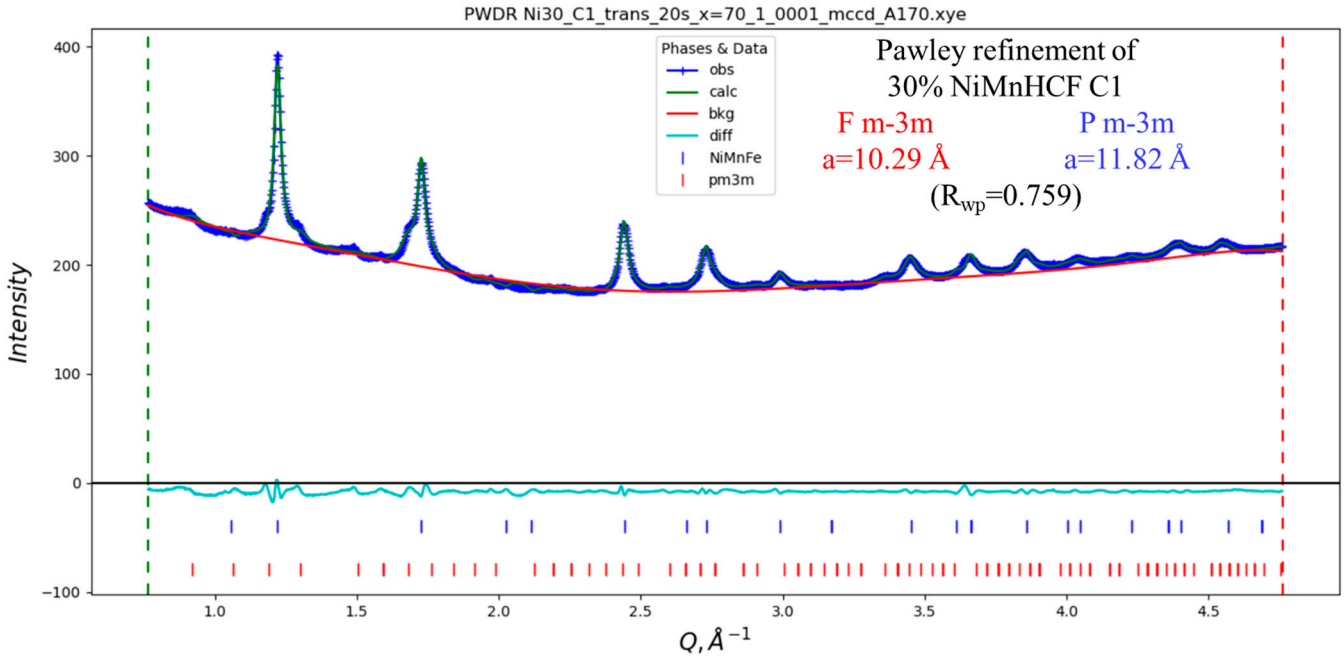

Figure S14. Pawley refinement of C1 of 30%NiMnHCF.

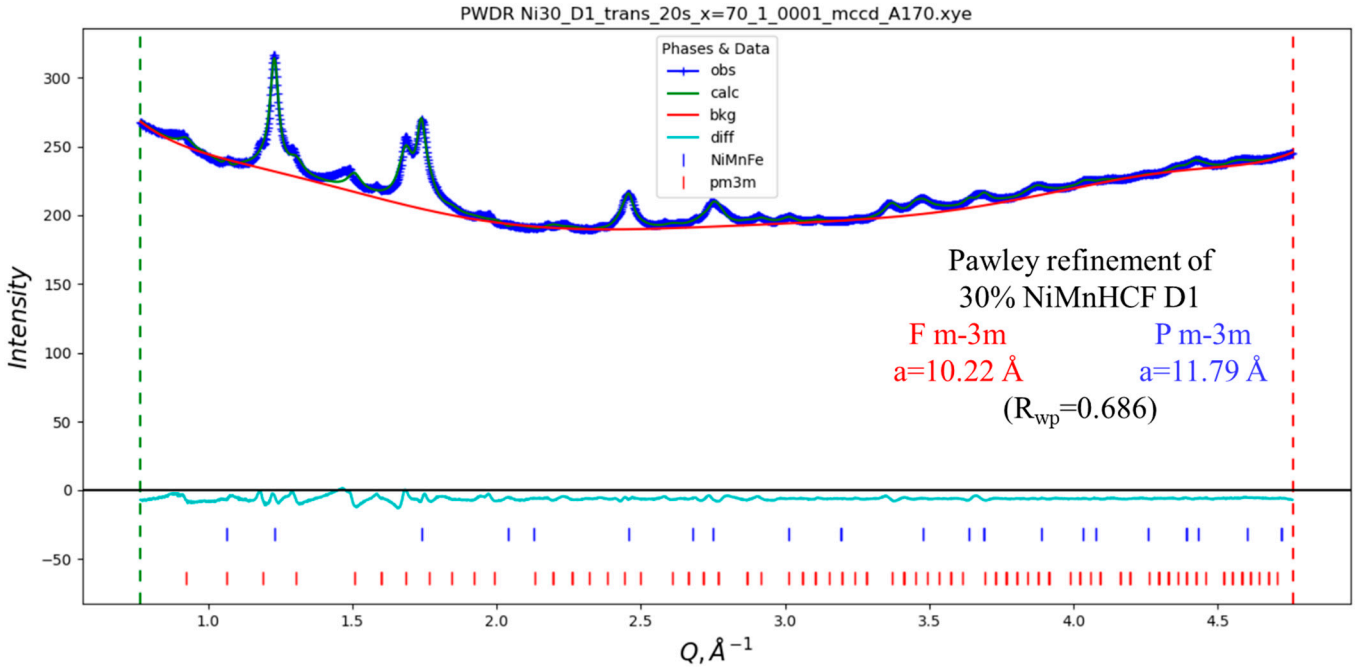

Figure S15. Pawley refinement of D1 of 30%NiMnHCF.

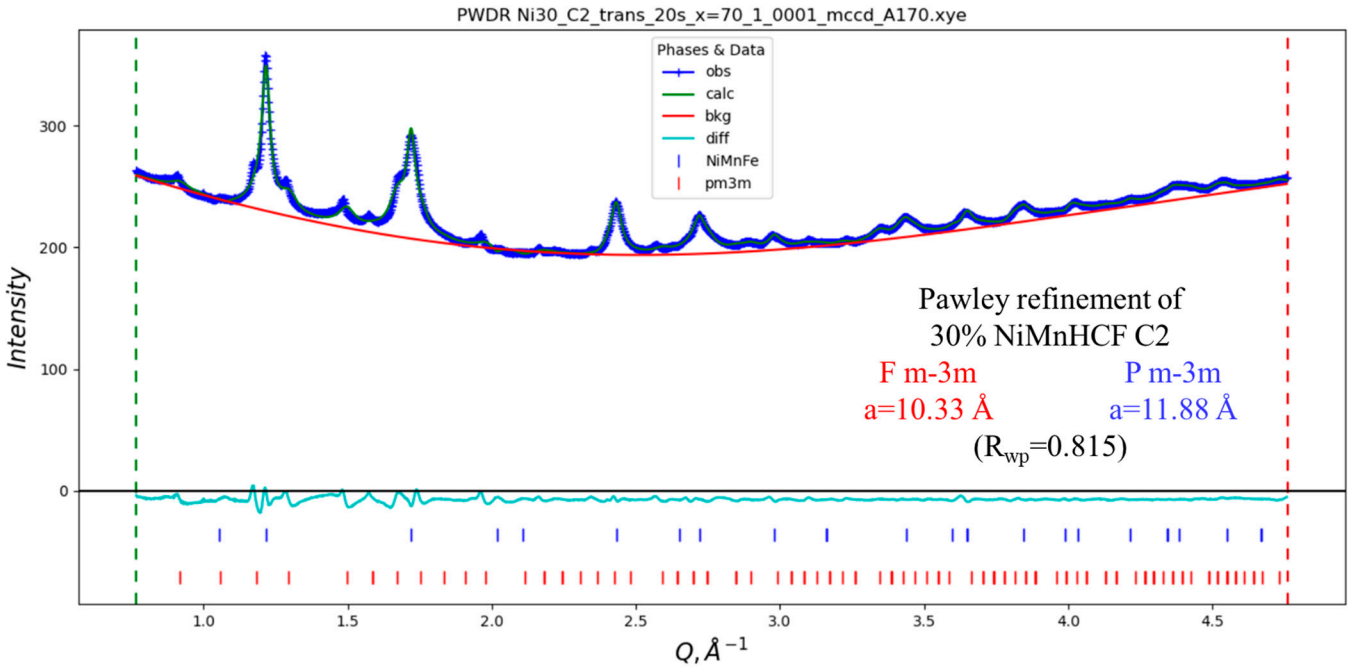

Figure S16. Pawley refinement of C2 of 30%NiMnHCF.

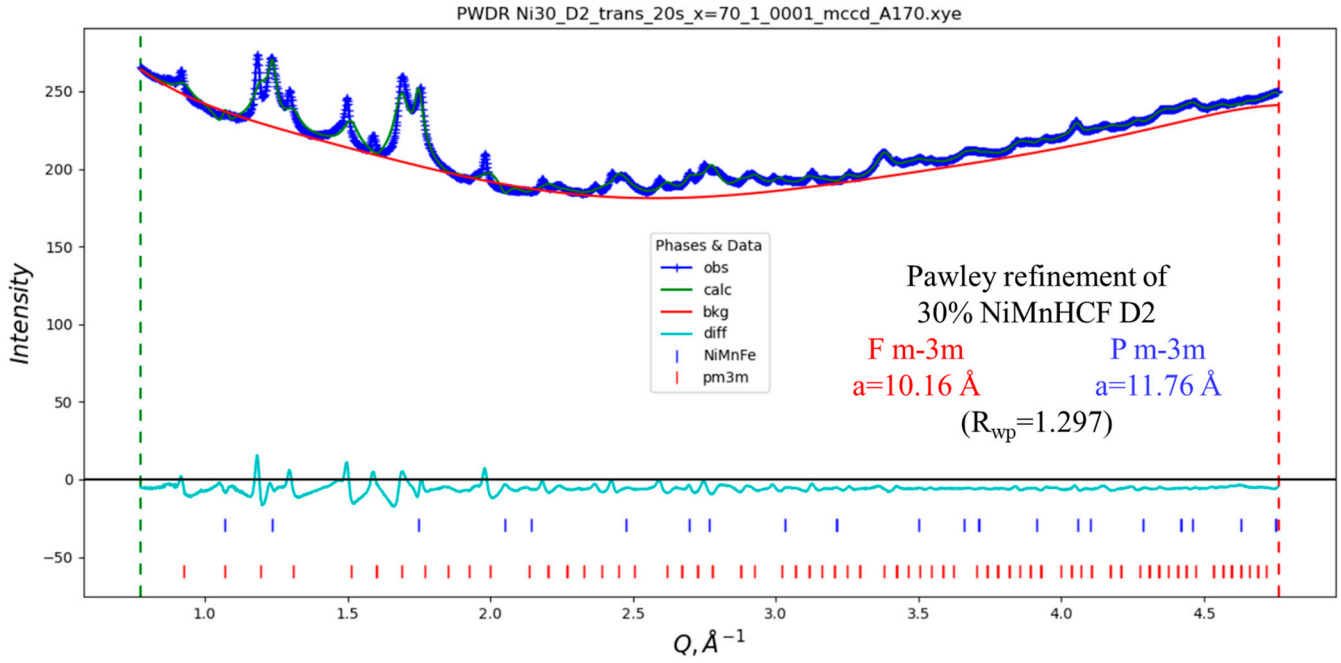

Figure S17. Pawley refinement of D2 of 30%NiMnHCF.

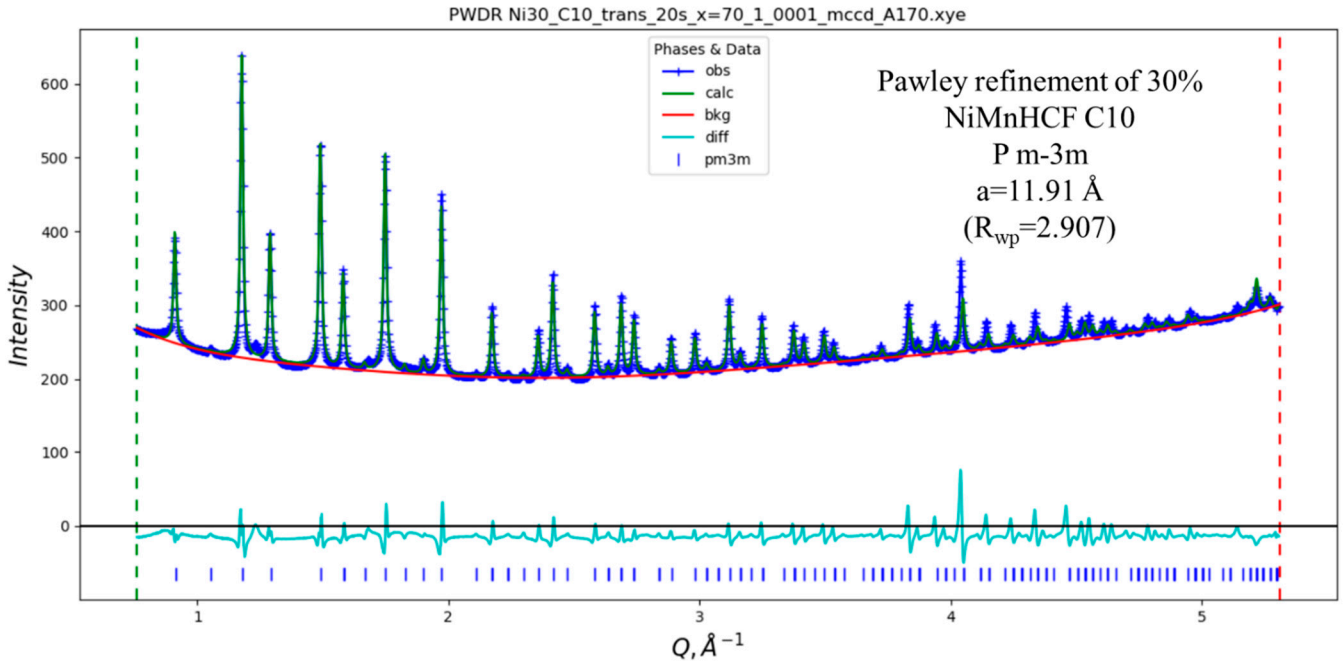

Figure S18. Pawley refinement of C10 of 30%NiMnHCF.

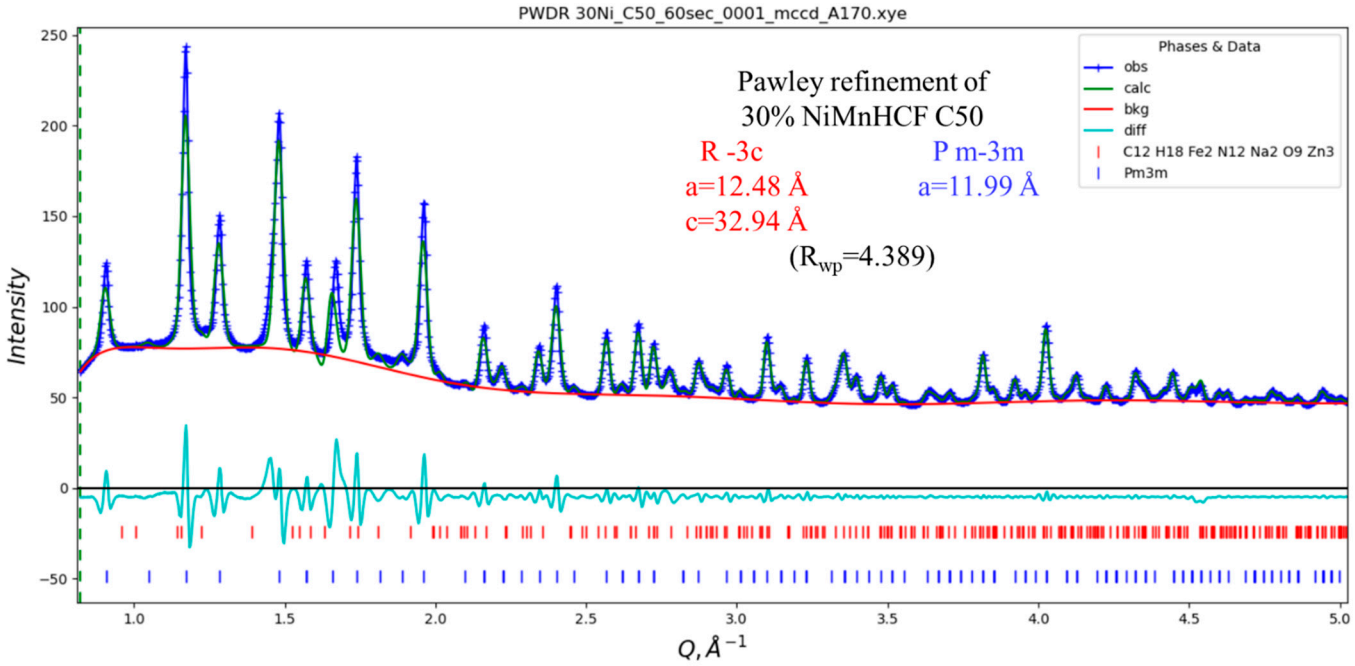

Figure S19. Pawley refinement of C50 of 30%NiMnHCF.

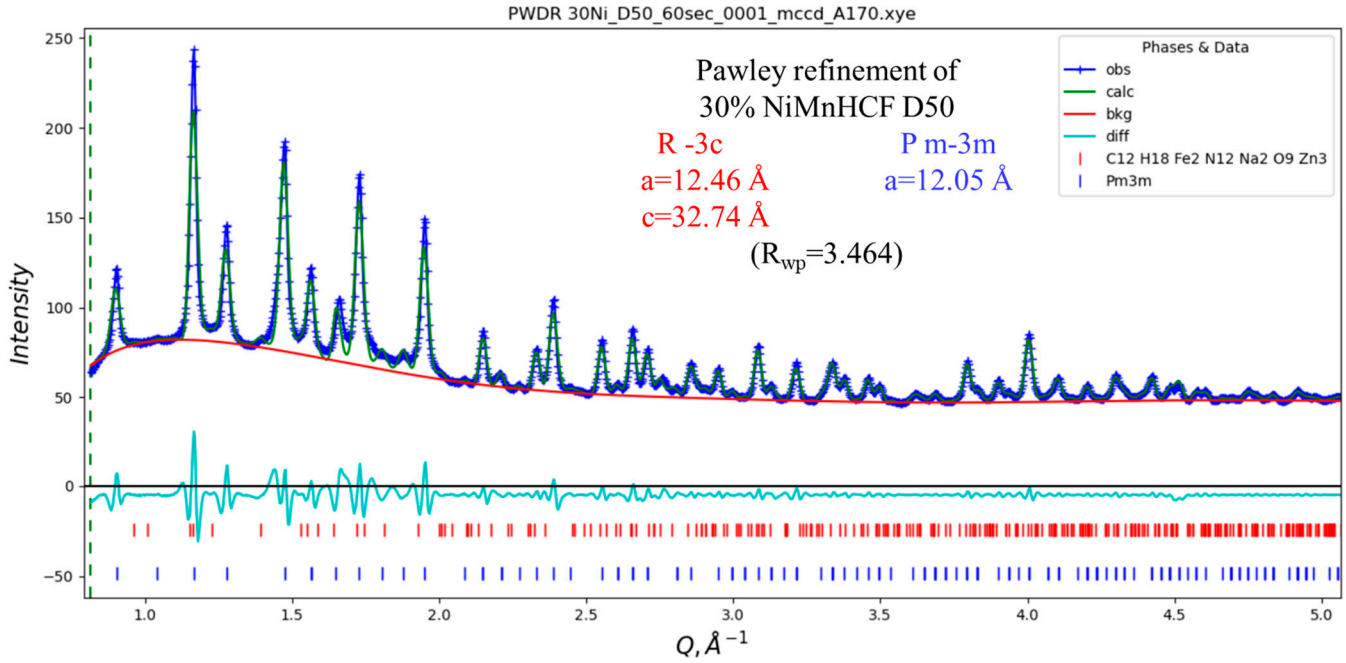

Figure S20. Pawley refinement of D50 of 30%NiMnHCF.

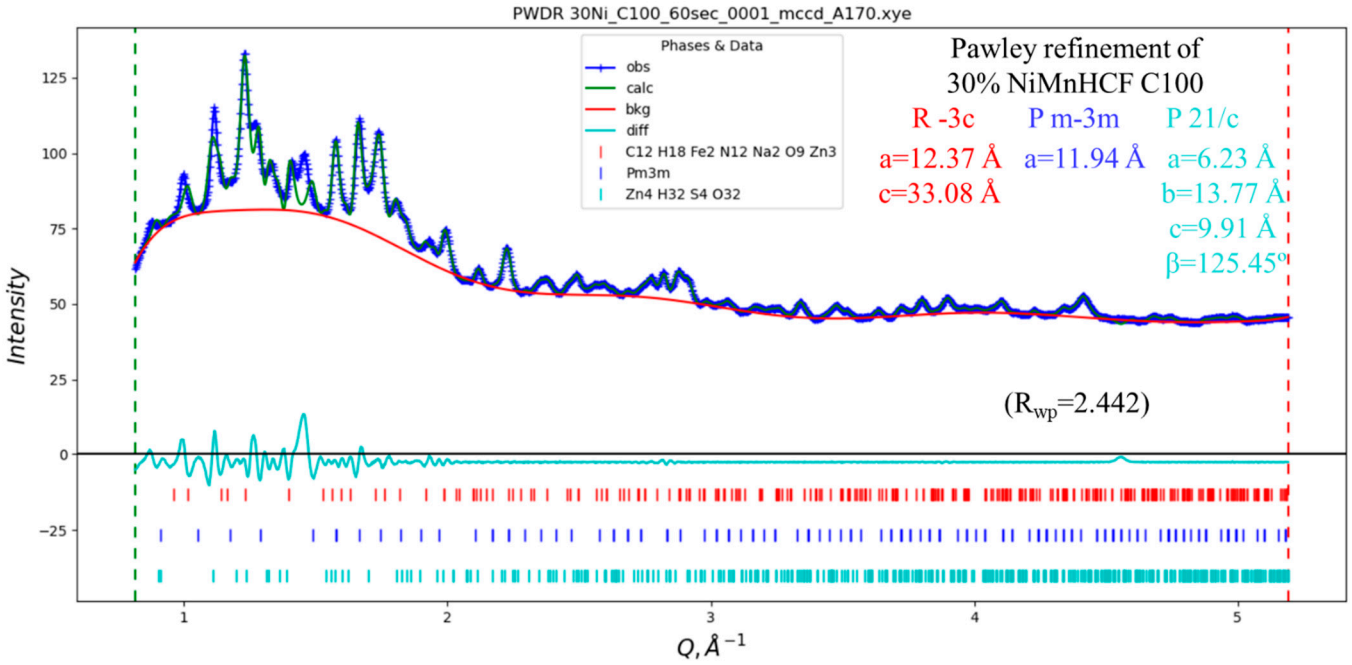

Figure S21. Pawley refinement of C100 of 30%NiMnHCF.

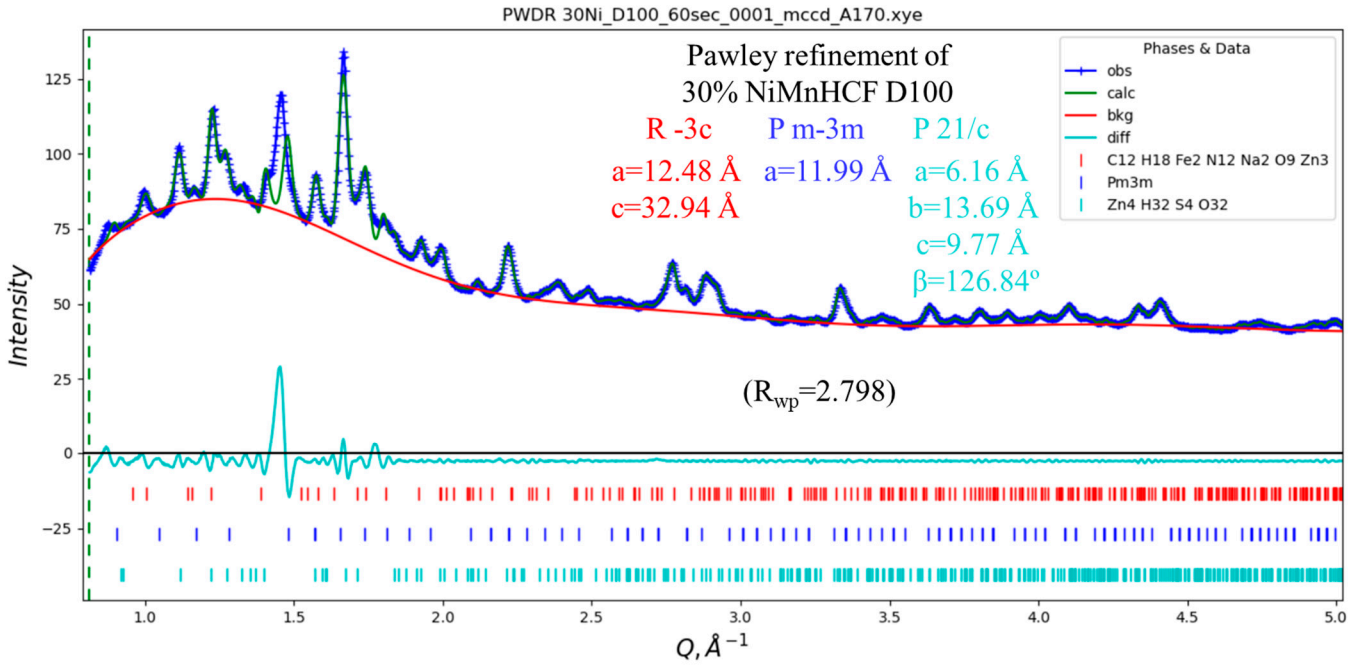

Figure S22. Pawley refinement of D100 of 30%NiMnHCF.