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Supporting Information

Structural regulation of P2-typed cathode via multi-cation doping for high-rate and stable sodium-ion batteries

Wenpei Kang, Ying Hu, Mengjia Han, Xiaoyu Fan, Daofeng Sun*

School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao, Shandong 266580, People's Republic of China

*Corresponding author. E-mail: wpkang@upc.edu.cn

Fig. S1. The optimized structures of (a) NMNO and (b) NMNCLFO based on the density functional theory (DFT) calculation. The DFT calculations were carried out using the Vienna Ab-initio Simulation Package (VASP) with the frozen-core all-electron projector-augment-wave (PAW) method. The Perdew-Burke-Ernzerhof (PBE) of generalized gradient approximation (GGA) was adopted to describe the exchange and correlation potential. The cutoff energy for the plane-wave basis set was set to 450 eV. A 2-layer 2×3 $Na_{0.7}Mn_{0.65}Ni_{0.35}O_2$(001) supercell (NMNO) was used. The vacuum region of 20 Å above them were added to ensure the decoupling between neighboring systems. Four Ni atoms in NMNO were radomly replaced with two Cu atom, one Li and one Fe atoms to simulate the model of $Na_{0.7}Mn_{0.65}Ni_{0.15}Cu_{0.12}Li_{0.03}Fe_{0.05}O_2$ (NMNCLFO). The geometry optimizations were performed until the forces on each ion was reduced below 0.01 eV/Å, and a 1×1×1 Gamma k-point sampling of the Brillouin zone was used. The van der Waals (vdW) interactions have been considered by using DFT-D3 method of Grimme.

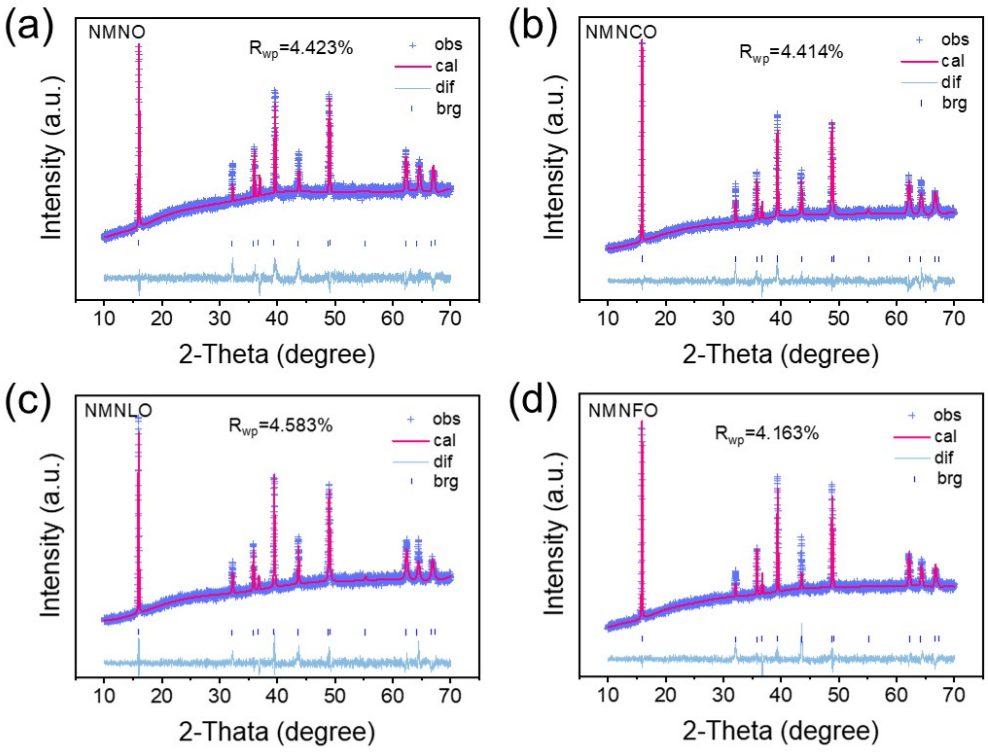

Fig. S2. Rietveld refinements of the XRD pattern for (a) NMNO, (b) NMNCO, (c)

NMNLO and (d) NMNFO.

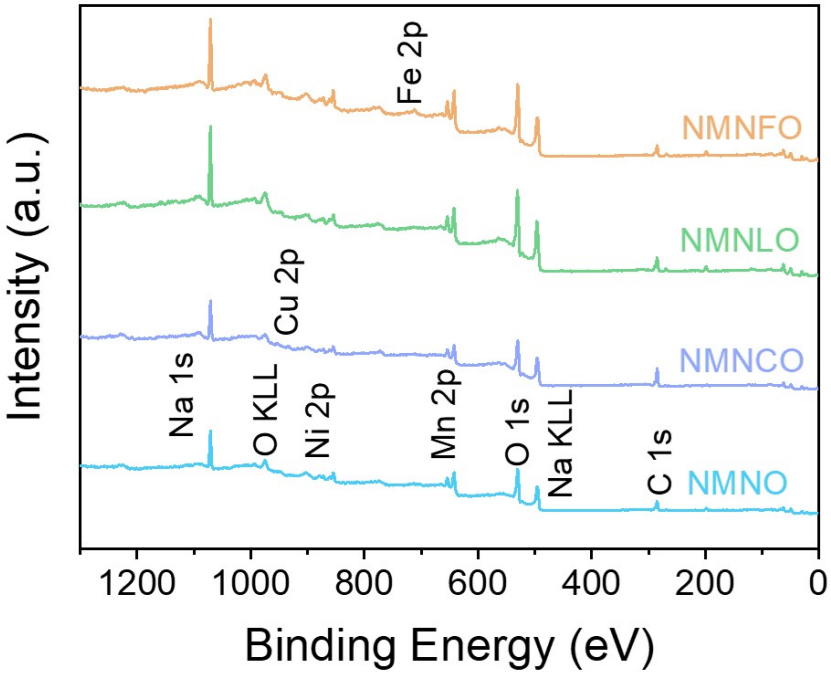

Fig. S3. The survey XPS spectra of NMNO, NMNCO, NMNLO and NMNFO.

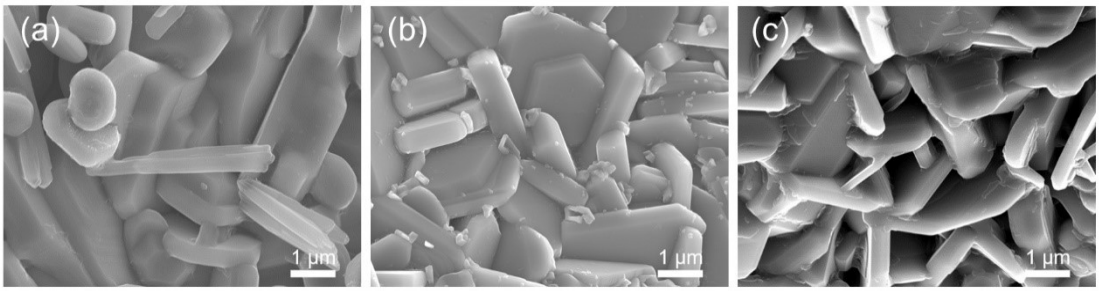

Fig. S4. SEM images of (a) NMNCO, (b) NMNLO, (c) NMNFO

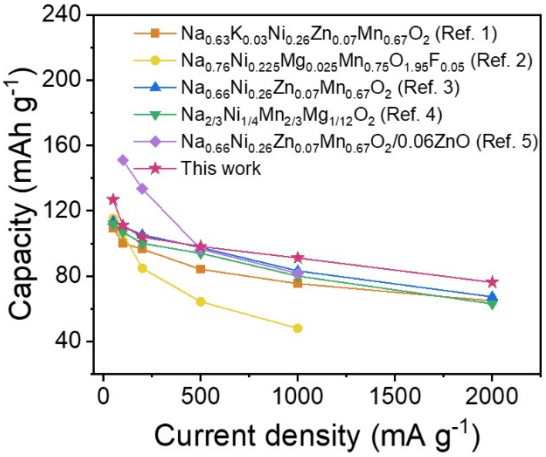

Fig. S5. Rate performance comparison between NMNCLFO and some other P2-type cathodes in the half cell.

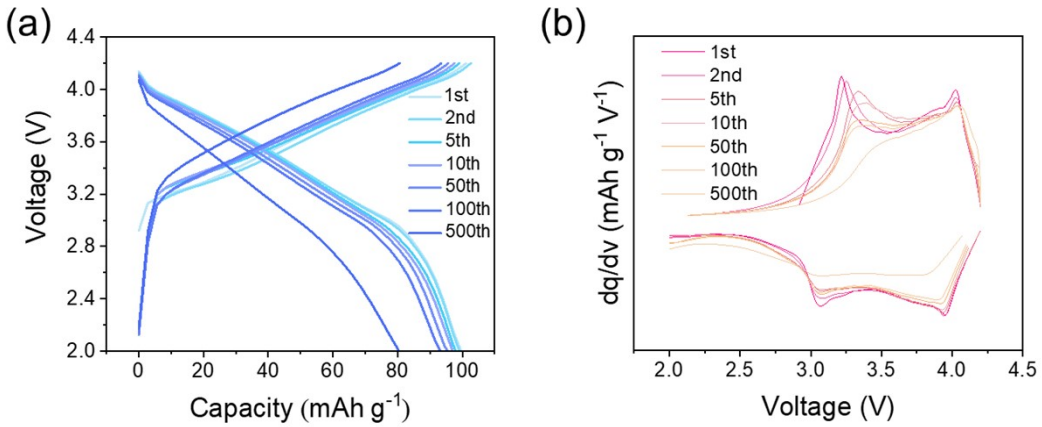

Fig. S6. (a) The selected charge-discharge profiles and (b) the related dQ/dV curves of NMNCLFO at current of 1.0 A g^{-1}.

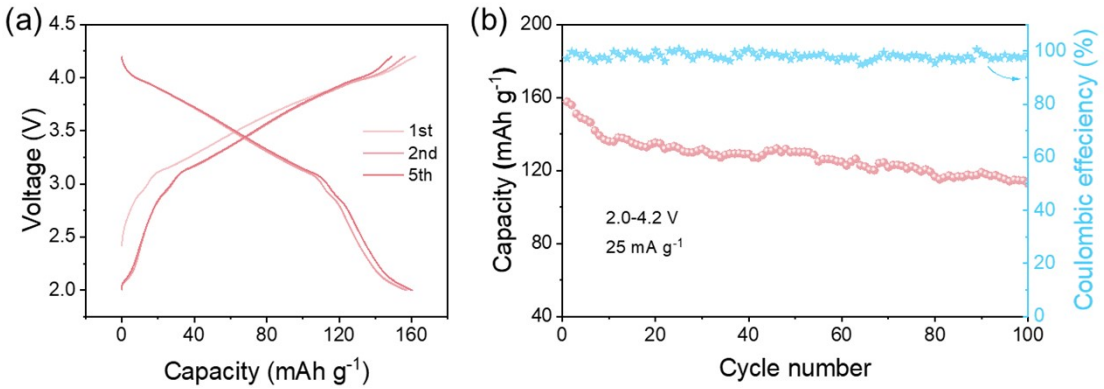

Fig. S7. (a) selected galvanostatic charge/discharge curves and (b) cycling performance of NMNCLFO cathode at 25 mA g^{-1}

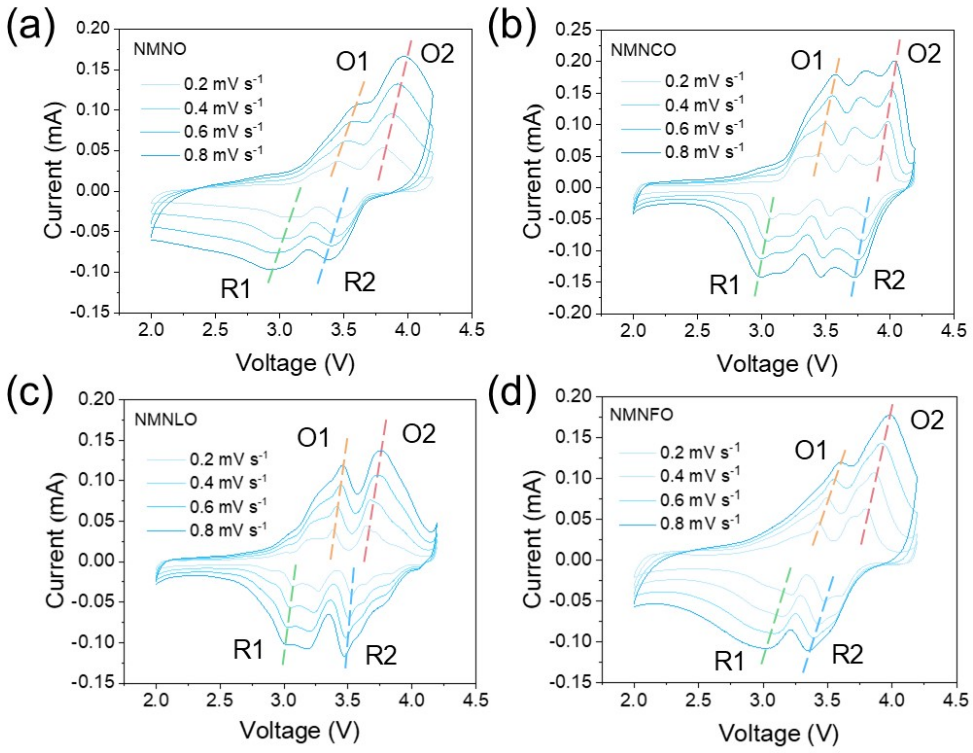

Fig. S8. CV curves of (a) NMNO, (b) NMNCO, (c) NMNLO, (d) NMNFO at different scan rates in the voltage range of 2.0-4.2 V.

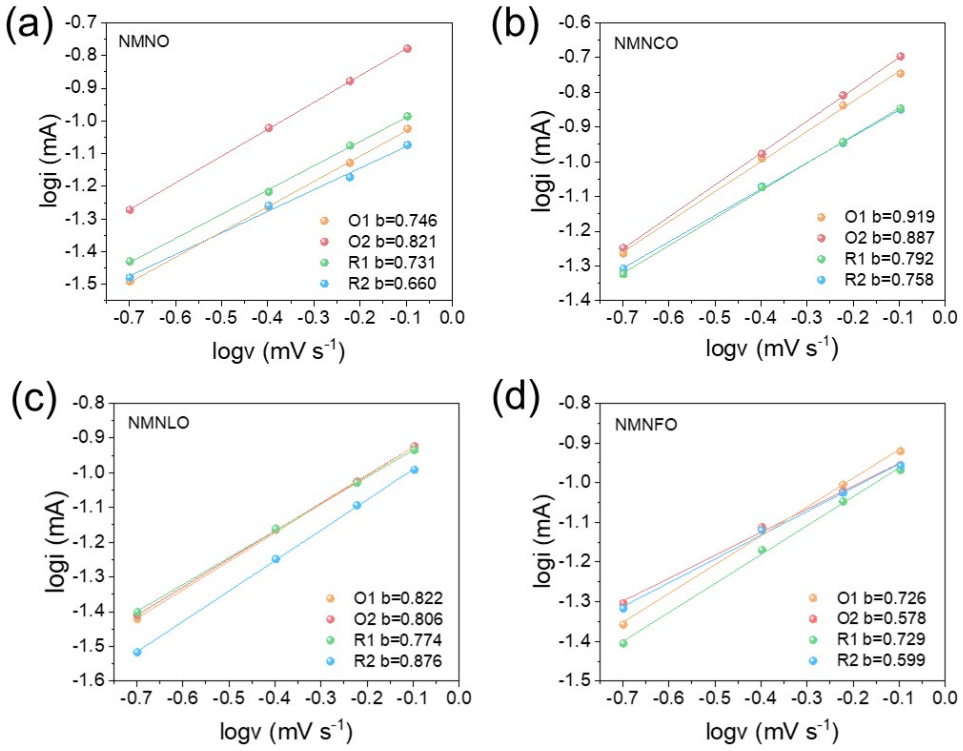

Fig. S9. The fitted straight lines between log (*v*) and log (*i*) for the (a) NMNO, (b) NMNCO, (c) NMNLO, (d) NMNFO.

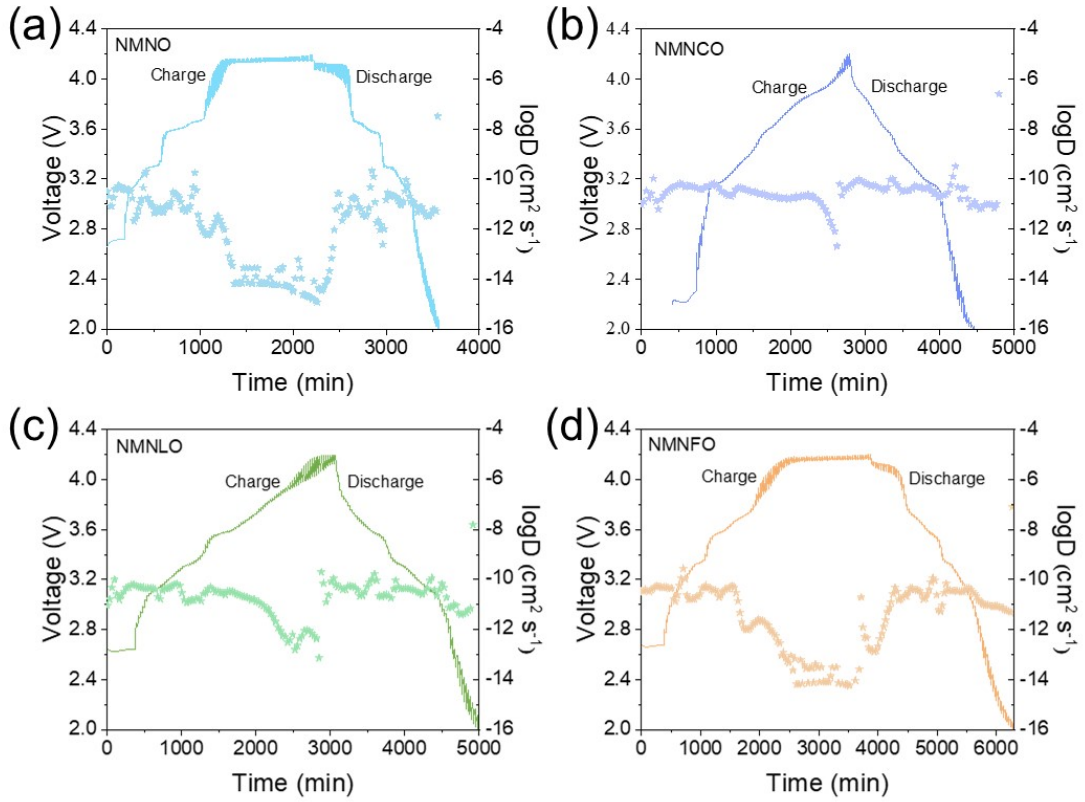

Fig. S10. GITT curves and the related D_{Na} values of (a) NMNO, (b) NMNCO, (c) NMNLO, and (d) NMNFO.

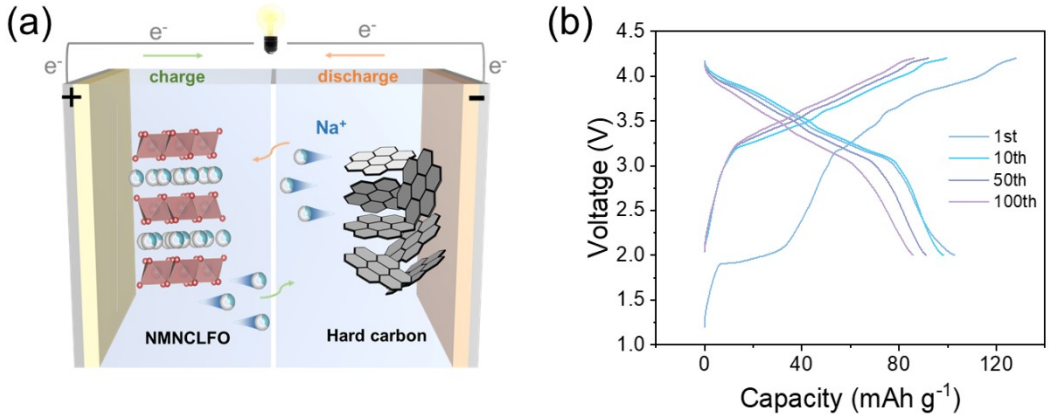

Fig. S11. (a) Schematic diagram of the configuration and (b) the selected charge-discharge profiles at 100 mA g^{-1} for the HC//NMNCLFO full cell.

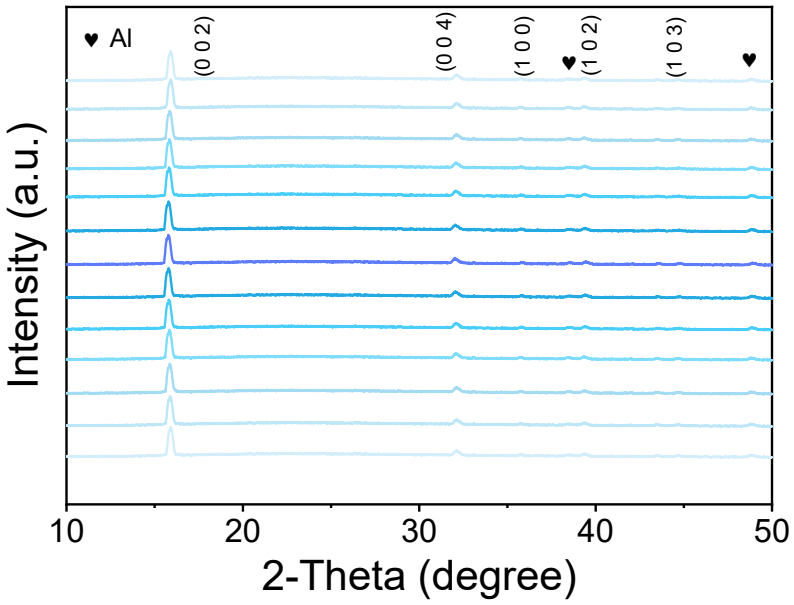

Fig. S12. *Ex-situ* XRD patterns of NMNCLFO at different desodiation/sodiation states in the first cycle.

Table S1. Crystallographic parameters of NMNO refined by the Rietveld method.

Space group = $P6_3/mmc$					
a=b=2.89112 Å, c=11.16403 Å, V=80.814 Å^3, R_{wp}=4.423%					
atom	**site**	**x**	**y**	**z**	**occupancy**
Na_e	2d	1/3	2/3	3/4	0.43
Na_f	2b	0	0	1/4	0.27
Mn	2a	0	0	0	0.65
Ni	2a	0	0	0	0.35
O	4f	1/3	2/3	0.09130	1

Table S2. Crystallographic parameters of NMNCO refined by the Rietveld method.

Space group = $P6_3/mmc$					
a=b=2.8988 Å, c=11.16842 Å, V=81. 057 Å^3, R_{wp}=4.414%					
atom	**site**	**x**	**y**	**z**	**occupancy**
Na_e	2d	1/3	2/3	3/4	0.41
Na_f	2b	0	0	1/4	0.29
Mn	2a	0	0	0	0.65
Ni	2a	0	0	0	0.23
Cu	2a	0	0	0	0.12
O	4f	1/3	2/3	0.09210	1

Table S3. Crystallographic parameters of NMNLO refined by the Rietveld method.

Space group = $P6_3/mmc$					
a=b=2.89157 Å, c=11.15947 Å, V=80.346 Å^3, R_{wp}=4.583%					
atom	**site**	**x**	**y**	**z**	**occupancy**
Na_e	2d	1/3	2/3	3/4	0.40
Na_f	2b	0	0	1/4	0.30
Mn	2a	0	0	0	0.65
Ni	2a	0	0	0	0.32
Li	2a	0	0	0	0.03
O	4f	1/3	2/3	0.08977	1

Table S4. Crystallographic parameters of NMNFO refined by the Rietveld method.

Space group = $P6_3/mmc$					
a=b=2.89662 Å, c=11.16541 Å, V=80.997 Å^3, R_{wp}=4.163%					
atom	**site**	**x**	**y**	**z**	**occupancy**
Na_e	2d	1/3	2/3	3/4	0.41
Na_f	2b	0	0	1/4	0.29
Mn	2a	0	0	0	0.65
Ni	2a	0	0	0	0.30
Fe	2a	0	0	0	0.05
O	4f	1/3	2/3	0.09346	1

Table S5. Crystallographic parameters of NMNO refined by the Rietveld method.

Space group = $P6_3/mmc$					
a=b=2.90618 Å, c=11.16618 Å, V=80.526 Å^3, R_{wp}=4.060%					
atom	**site**	**x**	**y**	**z**	**occupancy**
Na_e	2d	1/3	2/3	3/4	0.40
Na_f	2b	0	0	1/4	0.30
Mn	2a	0	0	0	0.65
Ni	2a	0	0	0	0.32
Cu	2a	0	0	0	0.12
Li	2a	0	0	0	0.03
Fe	2a	0	0	0	0.05
O	4f	1/3	2/3	0.09047	1

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