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Synthesis and characterization of mixed-valence manganese fluorophosphate and analogues with clathrate-like structures: $Mn^{III}_{6}F_{12}(PO_{3}(OH))_{8}[Na_{8}(K_{x}(H_{3}O)_{4-x}(H_{2}O)_{2})M^{IV}(OH)_{6}] \quad (M^{IV} = Mn, Ti, Ge)$

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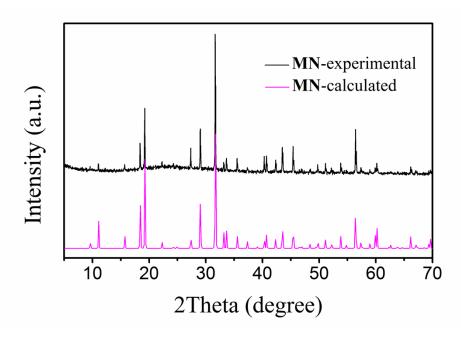


Figure S1 Comparison of the experimental and calculated PXRD patterns of MN.

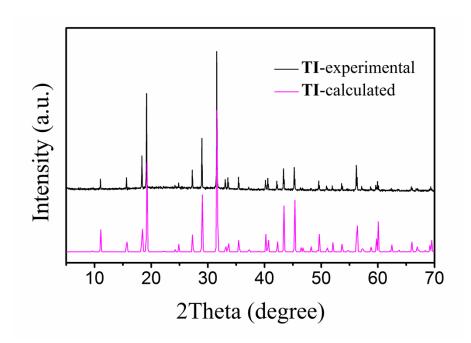


Figure S2 Comparison of the experimental and calculated PXRD patterns of TI.

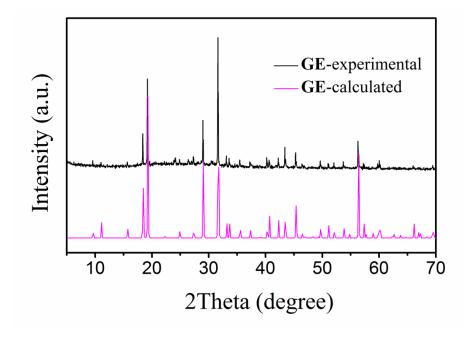
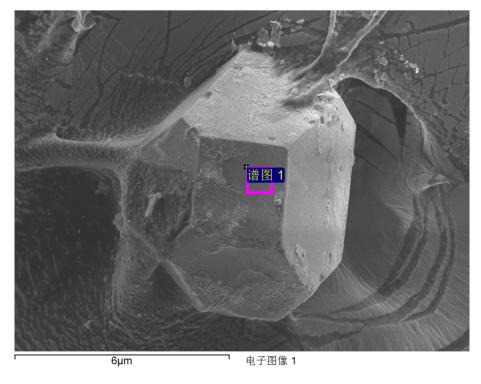


Figure S3 Comparison of the experimental and calculated PXRD patterns of GE.



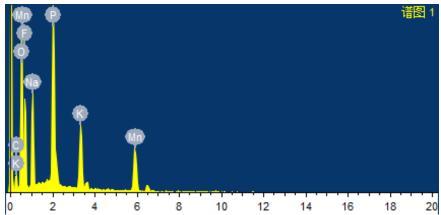


Figure S4 Scanning electron microscope image and EDS spectrum of \mathbf{MN} .

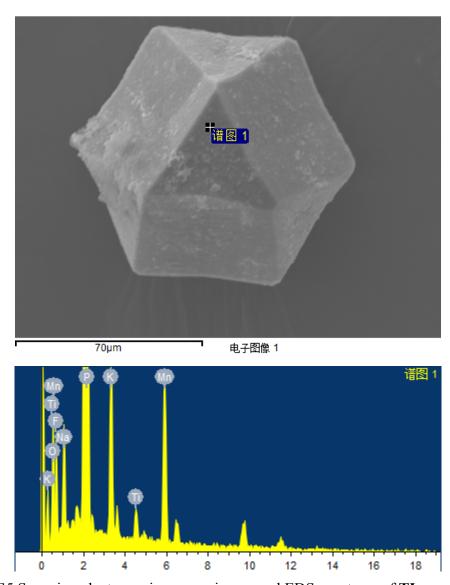


Figure S5 Scanning electron microscope image and EDS spectrum of TI

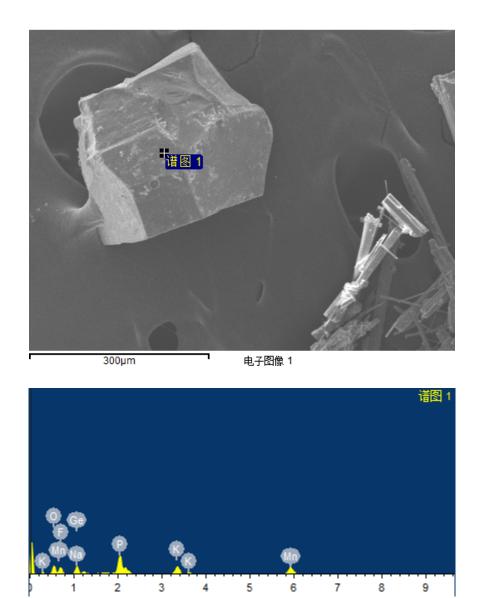


Figure S6 Scanning electron microscope image and EDS spectrum of GE.

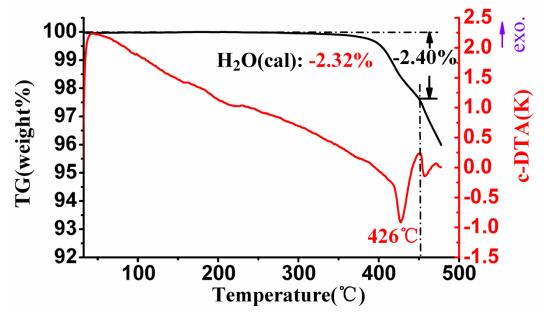


Figure S7 The TG-DTA curves of the compound MN

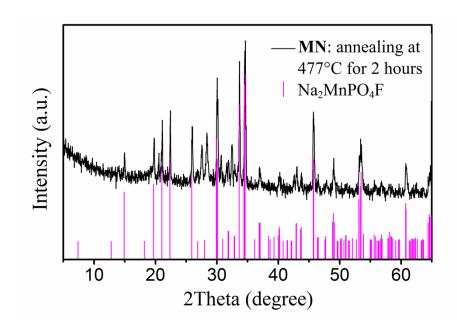


Figure S8 The PXRD pattern of MN after annealed at 477°C for 2h.

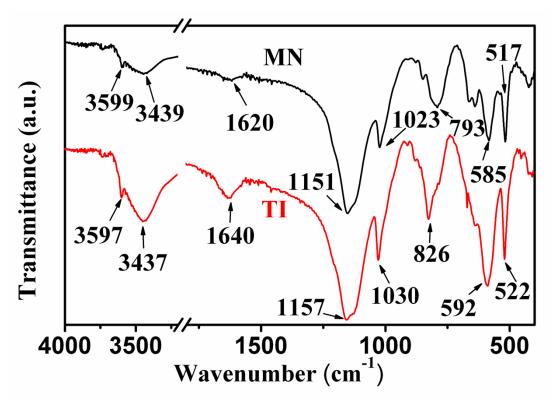


Figure S9 Comparison of FTIR spectra of the compounds MN and TI

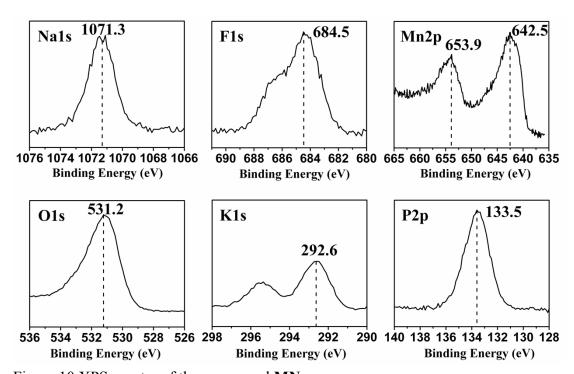


Figure 10 XPS spectra of the compound MN

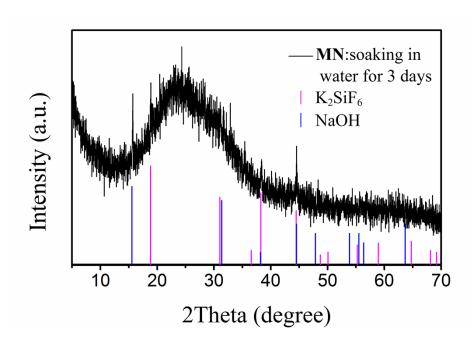


Figure S11 The PXRD pattern of MN after absorbed in water.