## Electronic Supplementary Information:

# Hydrothermal Growth of Facet-Tuneable Halide Perovskite Crystals $KMF_3$ (M= Mg, Mn, Co, Ni and Zn)

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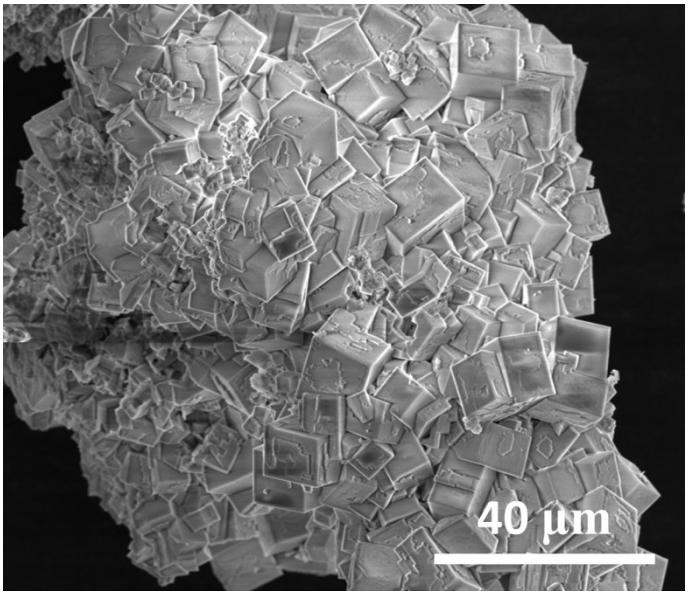


Fig. S1 SEM of $KNiF_3$ crystals with inter-connected blocks in hydrothermal condition.

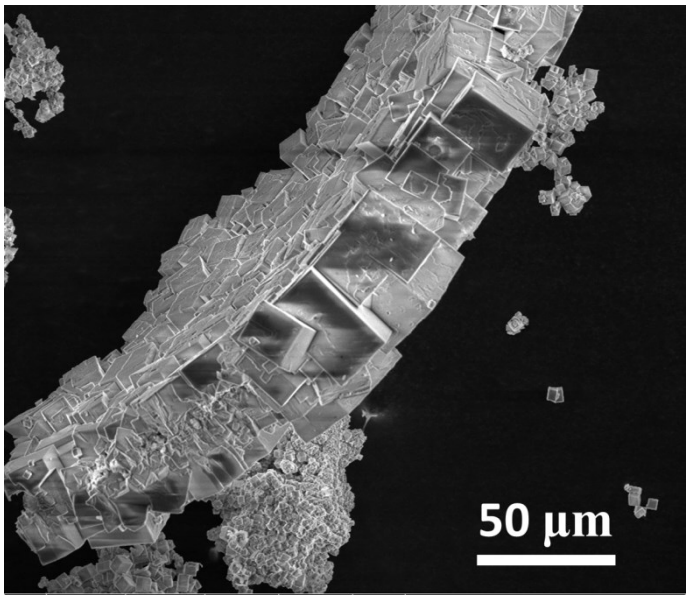


Fig. S2 SEM of $KNiF_3$ crystals with inter-locked mats in hydrothermal condition.

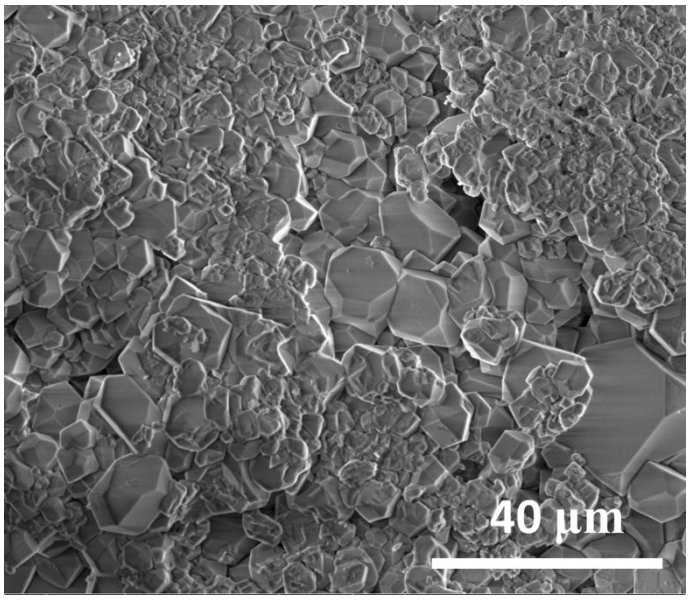


Fig. S3 SEM graph of aggregated $KZnF_3$ crystals in high concentration of reactants in hydrothermal condition.

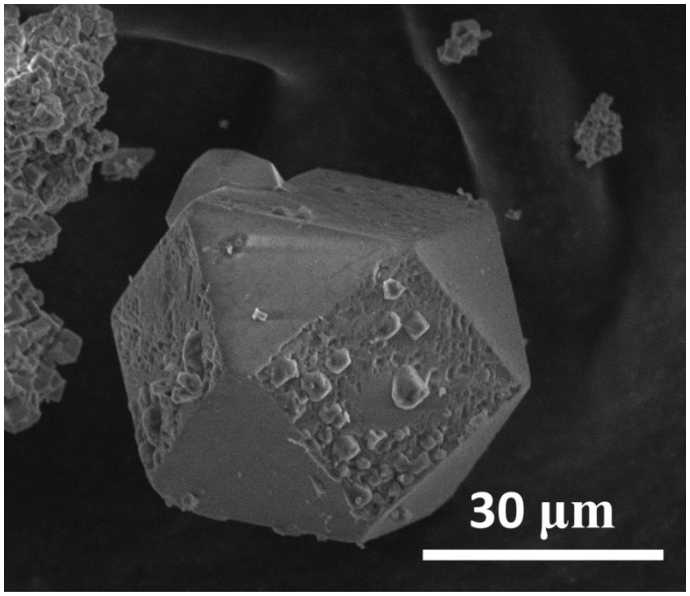


Fig. S4 SEM graph of $KZnF_3$ with small sized twin crystals on the pit at these facets obtained in hydrothermal condtion.

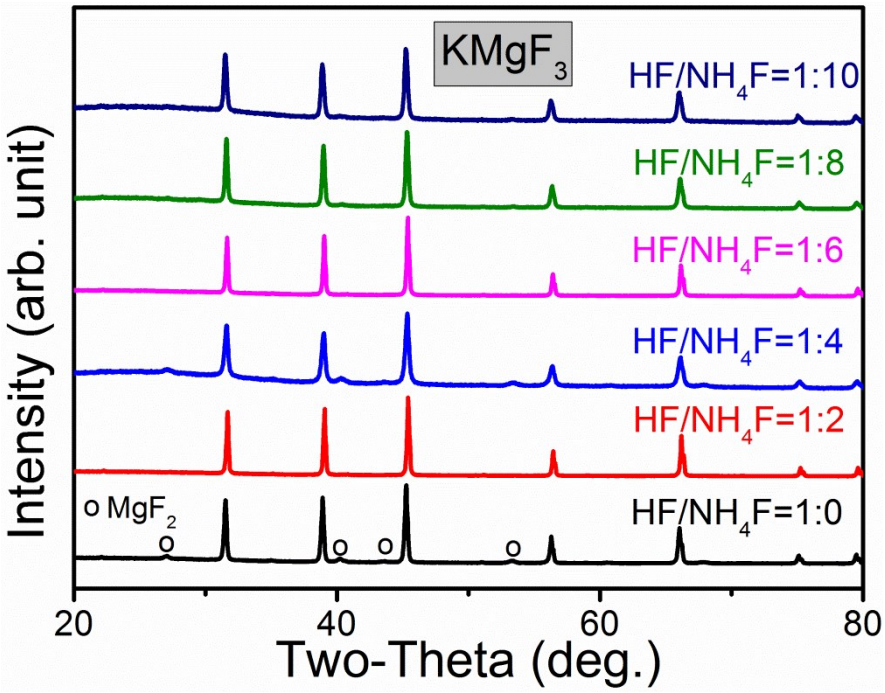


Fig. S5 XRD of hydrothermal synthesized $KMgF_3$ crystal with tuneable mineralizer ratio of $HF/NH_4F$ from 1:0 to 1:10. Black circles in the data of $HF/NH_4F$=1:0 indicate the diffraction peak positions of $MgF_2$ impurity.

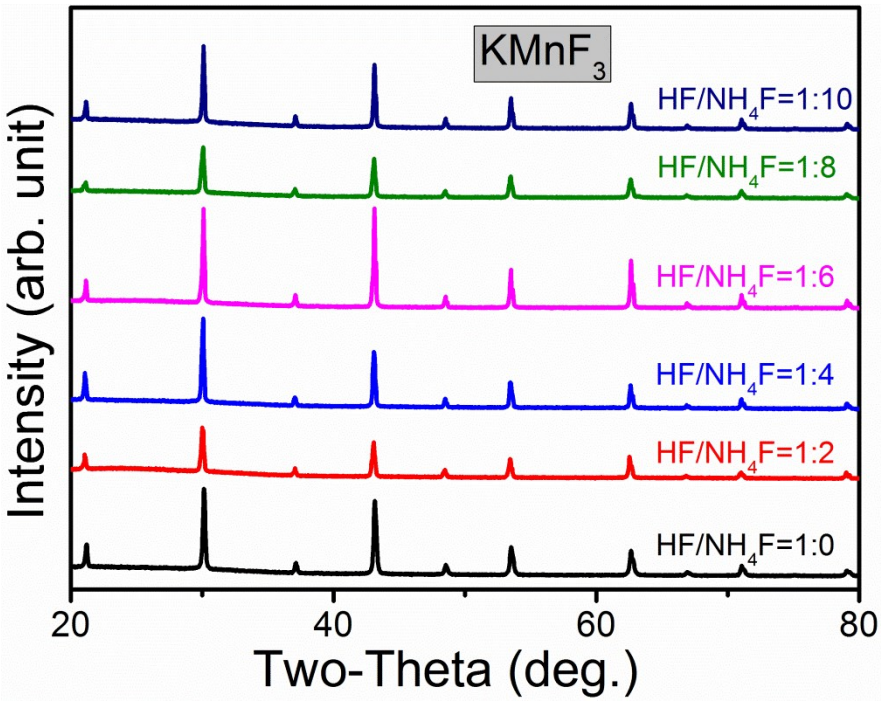


Fig. S6 XRD of $KMnF_3$ samples synthesized via hydrothermal method with varied $HF/NH_4F$ ratio.

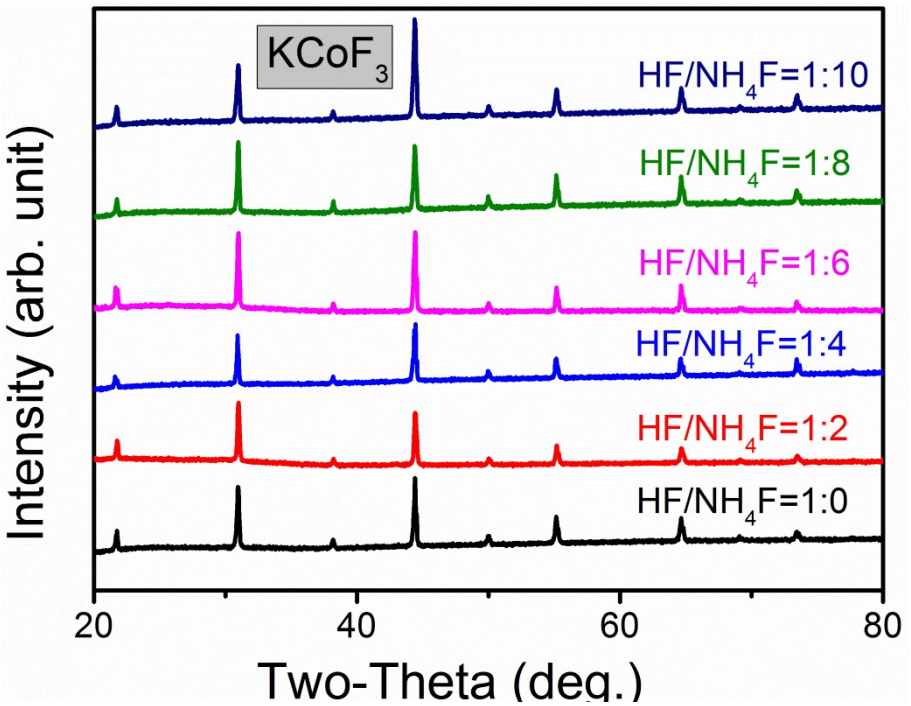


Fig. S7 XRD of $KCoF_3$ samples synthesized via mild hydrothermal method with tuneable $HF/NH_4F$ ratio from 1:0 to 1:10.

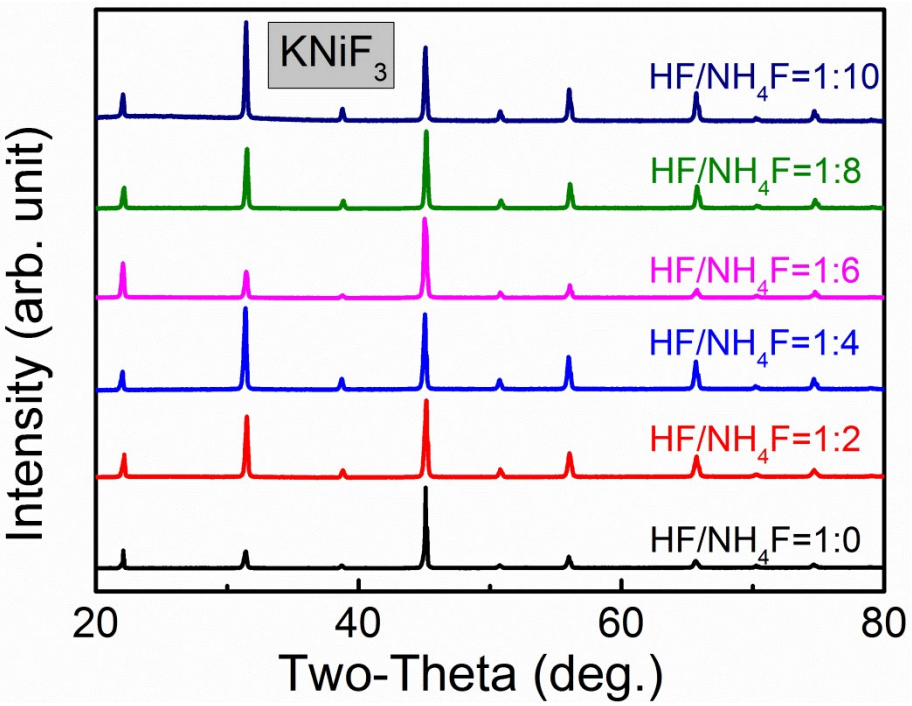


Fig. S8 XRD of $KNiF_3$ samples synthesized via mild hydrothermal method with tuneable $HF/NH_4F$ ratio from 1:0 to 1:10.

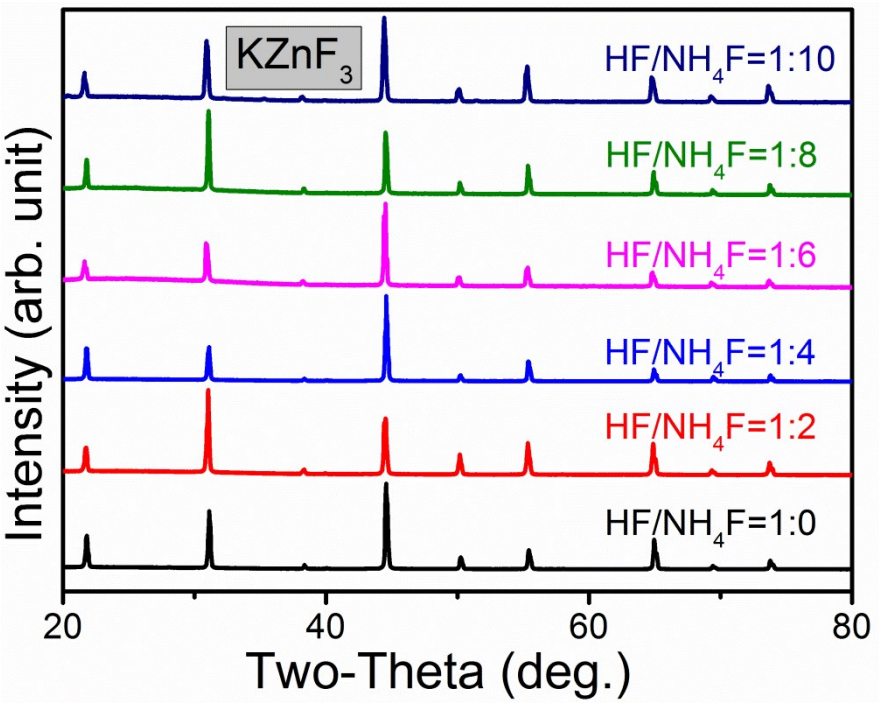


Fig. S9 XRD of $KZnF_3$ samples synthesized via mild hydrothermal method with tuneable $HF/NH_4F$ ratio from 1:0 to 1:10.

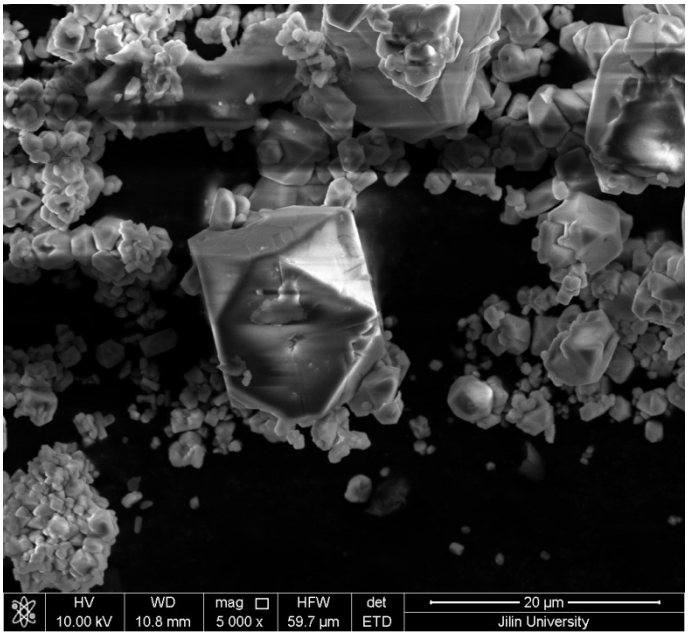


Fig. S10 SEM graph of $KFeF_3$ synthesized via hydrothermal method with the ratio of $HF/NH_4F$ is 1:4.

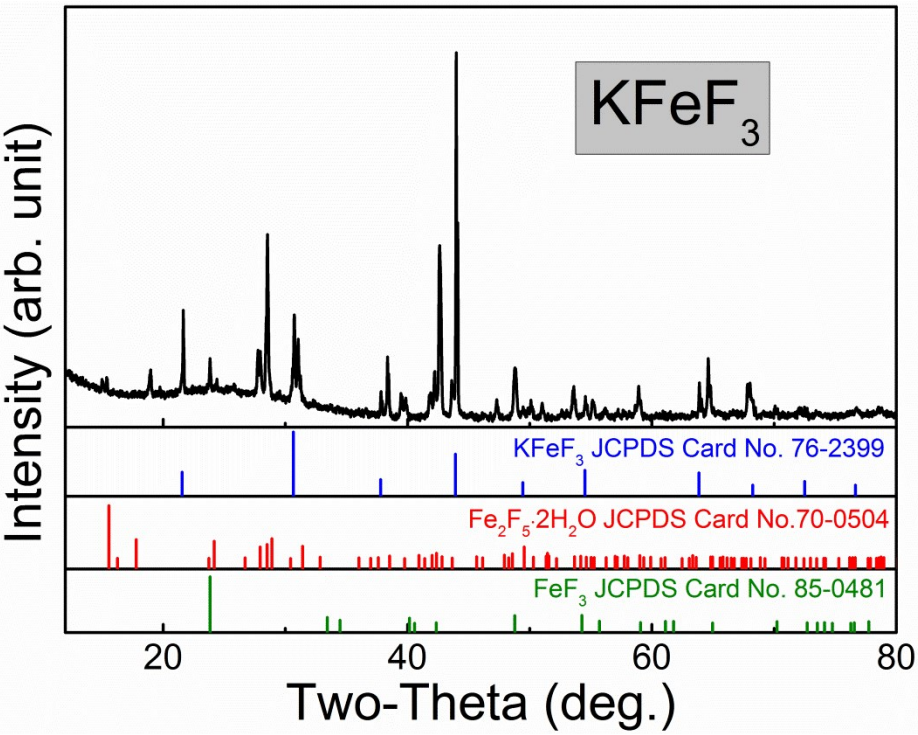


Fig. S11 XRD of $KFeF_3$ sample synthesized via similar method of other $KMF_3$. Perovskite phase could be indexed according to the JCPDS Card No. 76-2399, and other impurity phases can be indexed as shown in the red and green bars for $Fe_2F_5·2H_2O$ (JCPDS Card No. 70-0504) and $FeF_3$ (JCPDS Card No. 85-0481), respectively.

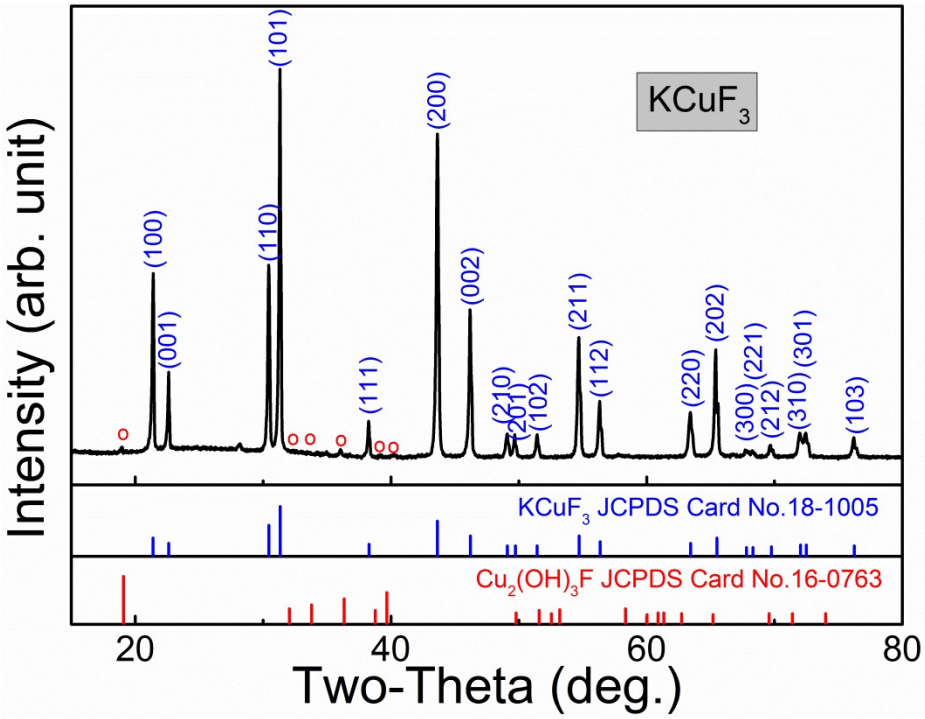


Fig. S12 XRD of hydrothermally synthesized $KCuF_3$ sample with $Cu_2(OH)_3F$ impurity phase. Open circle and red bars indicate the diffraction peak positions in the data.

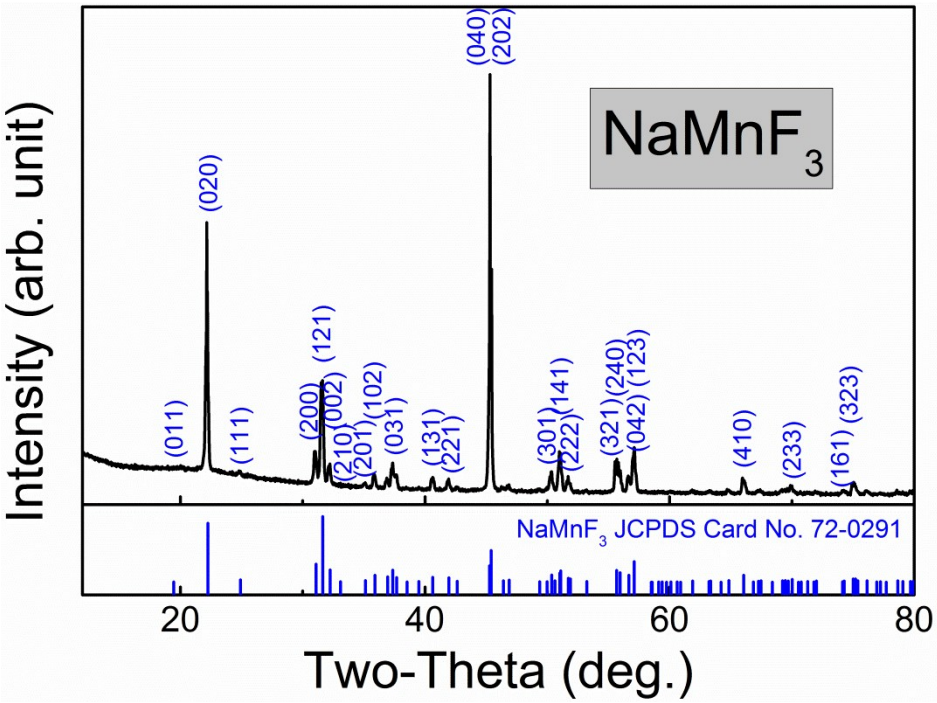


Fig. S13 XRD of $NaMnF_3$ sample that crystalized into Pnma space group with the JCPDS Card No. 72-0291.

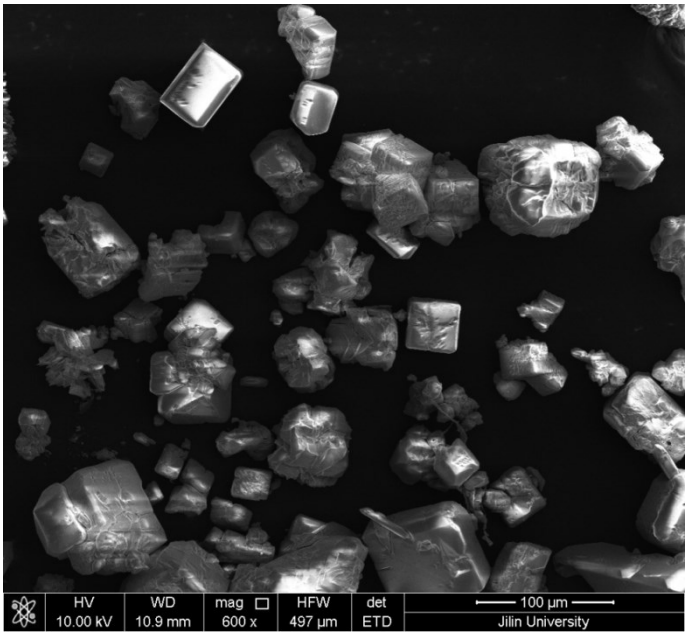


Fig. S14 SEM graph of $NaMnF_3$ synthesized via mild hydrothermal method, respectively.

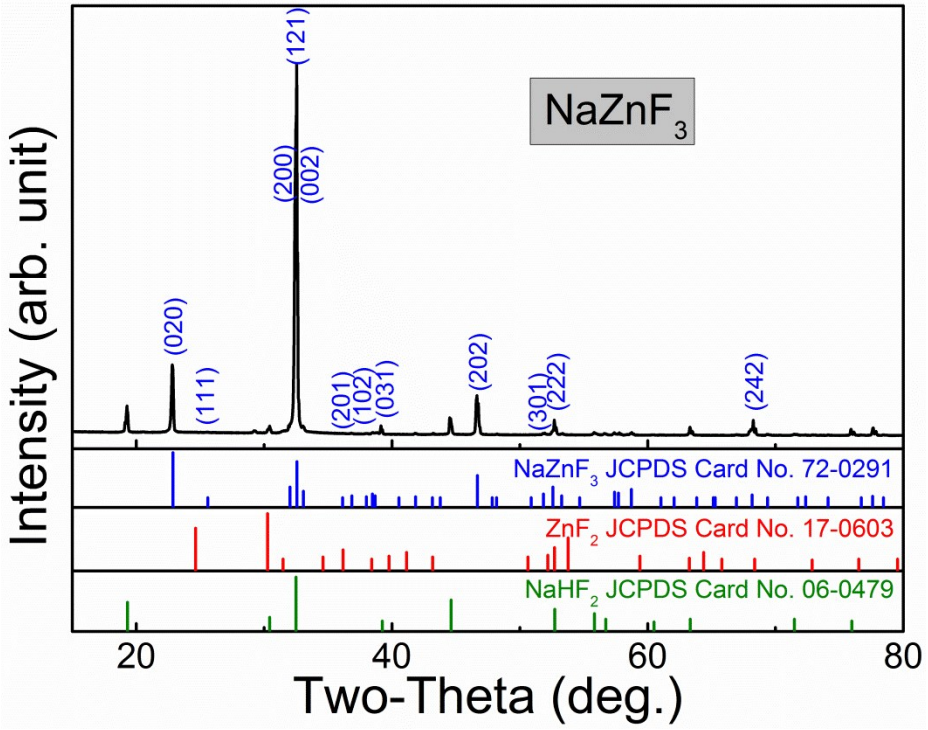


Fig. S15 XRD of $NaZnF_3$ sample synthesized via mild hydrothermal method with impurities of $ZnF_2$ and $NaHF_2$ phases.

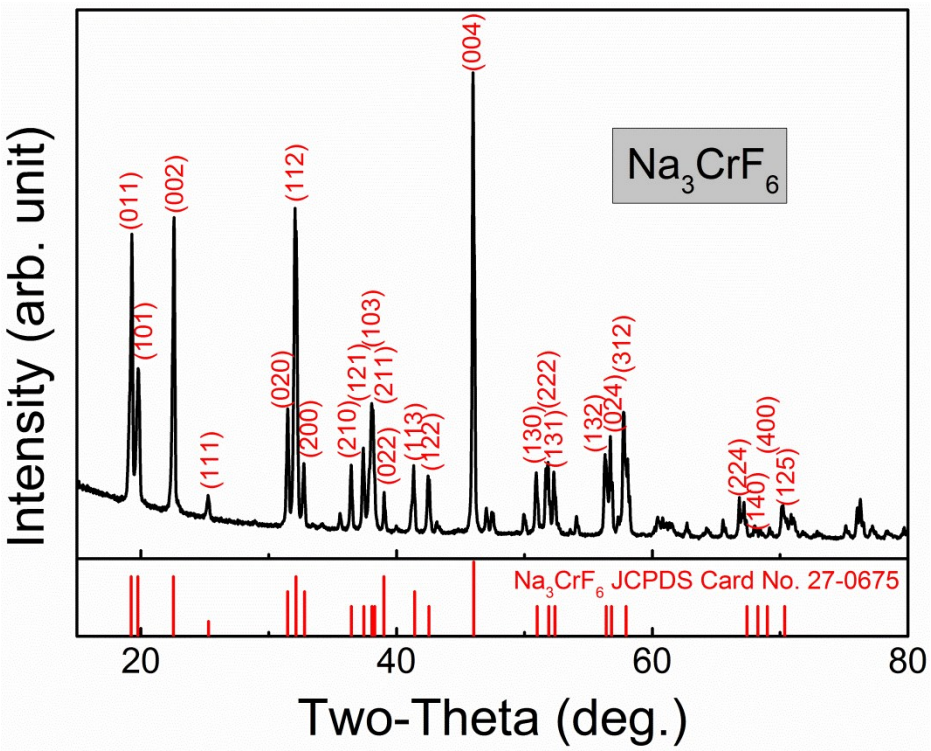


Fig. S16 $Na_3CrF_6$ phase was obtained rather than perovskite $NaCrF_3$ phase as intended in the same synthetic procedure of hydrothermal route.

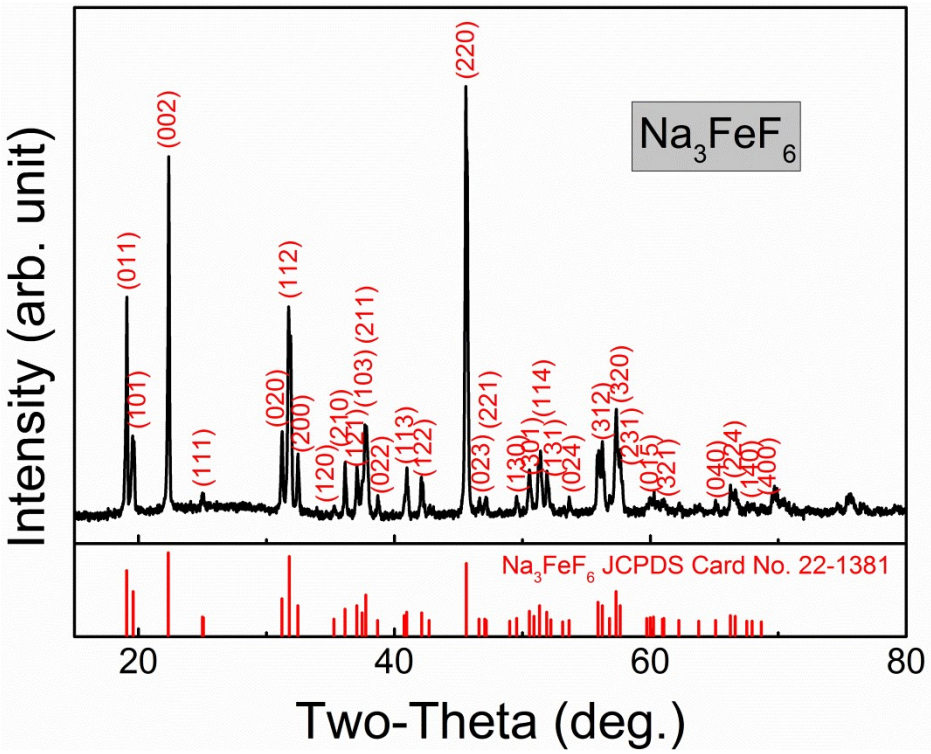


Fig. S17 $Na_3FeF_6$ phase was obtained rather than perovskite $NaFeF_3$ phase as intended in the same synthetic procedure of hydrothermal route.

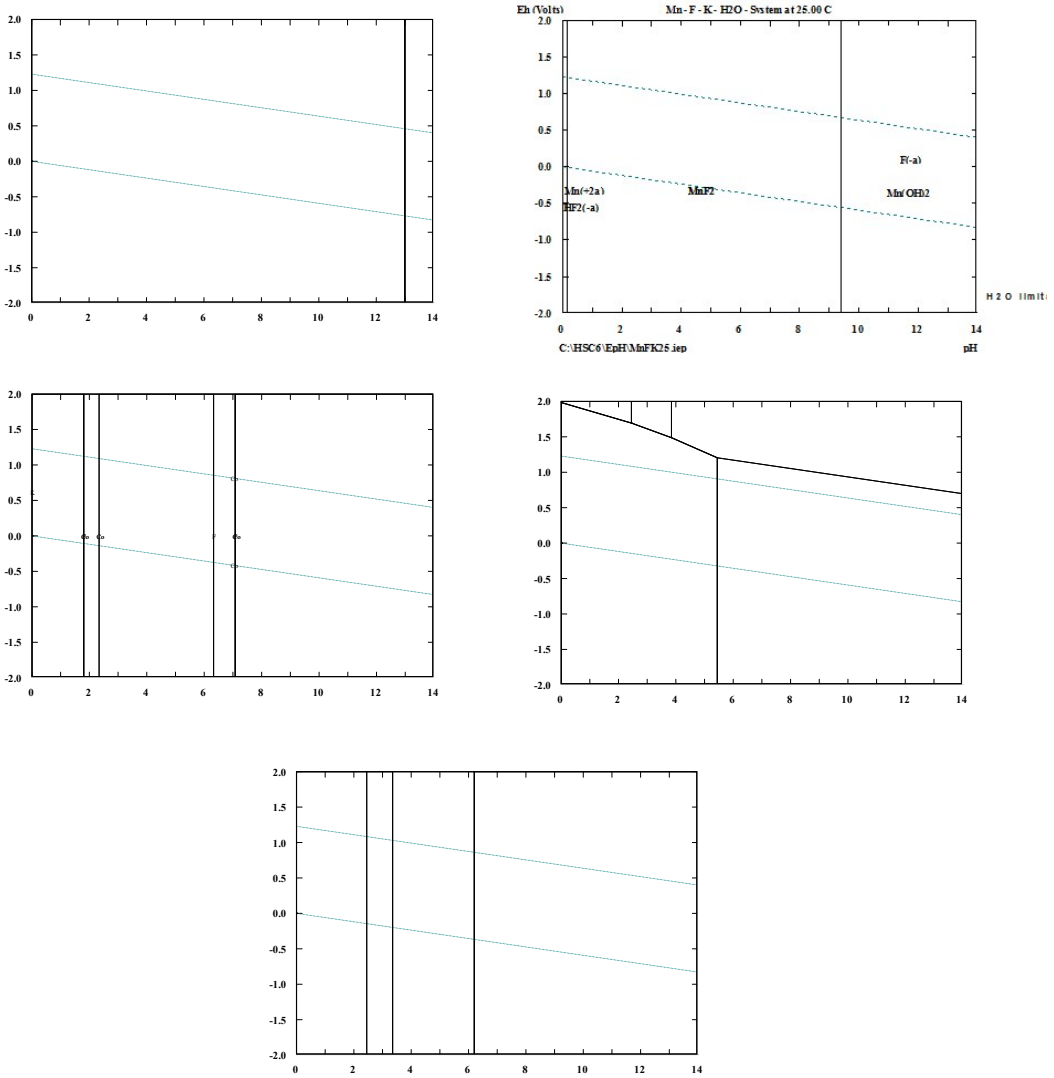


Fig. S18 Simulated Pourbaix (E-pH) diagram of M-F-K-$H_2O$ system at room temperature (25 $^oC$) with the respective thermodynamic data of all possible species based on HSC Chemistry 6.0 software.

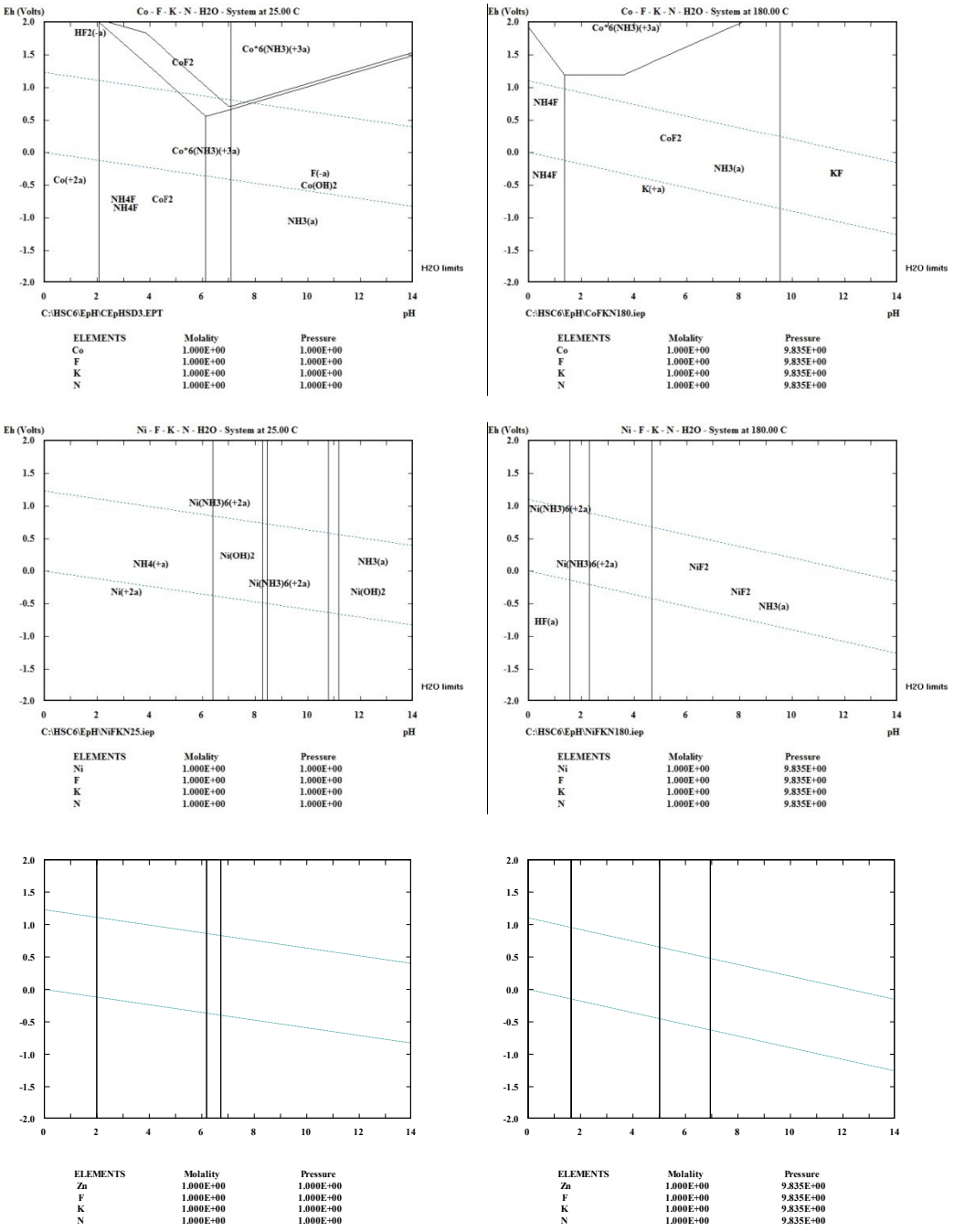


Fig. S19 Comparison of the stable species of Co and Zn in M-F-K-N-$H_2O$ system at room temperature and 180 $^oC$ in hydrothermal condition.

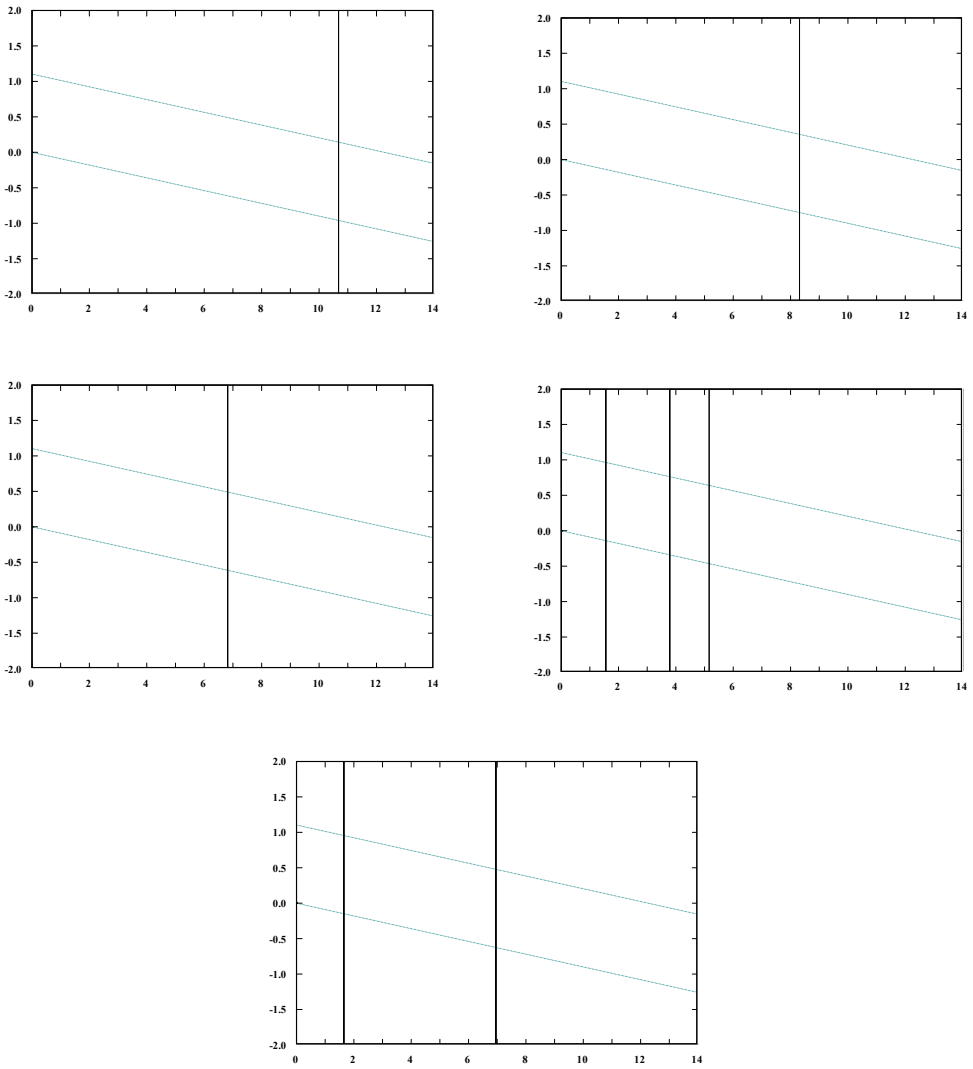


Fig. S20 Simulated Pourbaix (E-pH) diagram of M-F-K-$H_2O$ system at hydrothermal condition (180 $^oC$) with the respective thermodynamic data of all possible species based on HSC Chemistry 6.0 software.