**Catalysis of the Thermal Decomposition of Transition Metal Nitrate Hydrates by Poly(vinylidene difluoride)**

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**Supporting Information**

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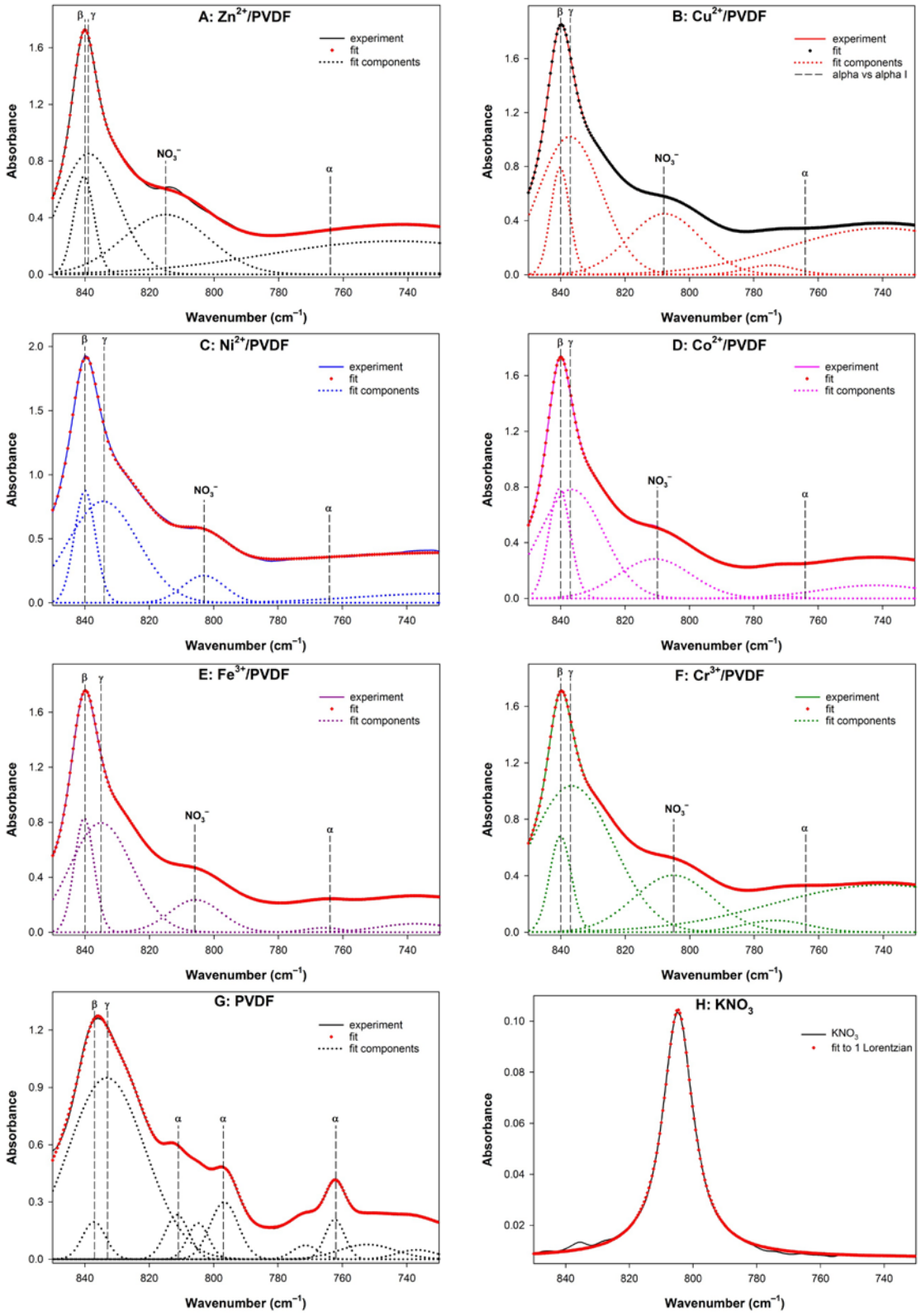


**Figure S1**. Deconvoluted IR data of room temperature PVDF-doped/ undoped thin films at 850-720 $cm^{-1}$ region to identify the effect from nitrate peak. **A** $Zn^{2+}$/ PVDF; **B** $Cu^{2+}$/ PVDF; **C** $Ni^{2+}$/ PVDF; **D** $Co^{2+}$/ PVDF; **E** $Fe^{3+}$/ PVDF; **F** $Cr^{3+}$/ PVDF; **G** PVDF; **H** $KNO_3$. The α-, β-, γ-phase, and $NO_3^-$ marker peaks are labeled.

**Table S1**. Peak maxima and linewidths found from deconvolution of IR spectra at room temperature. The spectra are fit to Gaussian functions with the reported linewidths being the full width at half maximum. The uncertainties on all of the fits are ±1 $cm^{-1}$ or less.

| Sample | C=O region Peak 1 | | | C=O region Peak 2 | | | $NO_3^-$ region | |
|---|---|---|---|---|---|---|---|---|
| | Peak maximum ($cm^{-1}$) | Linewidth ($cm^{-1}$) | Relative Intensity | Peak maximum ($cm^{-1}$) | Linewidth ($cm^{-1}$) | Relative Intensity | Peak maximum ($cm^{-1}$) | Linewidth ($cm^{-1}$) |
| $Zn^{2+}$/PVDF | 1639 | 28 | 0.21 | 1657 | 12 | 0.80 | 815 | 16 |
| $Cu^{2+}$/PVDF | 1635 | 30 | 0.47 | 1656 | 11 | 0.58 | 808 | 13 |
| $Ni^{2+}$/PVDF | 1633 | 38 | 0.64 | 1655 | 10 | 0.39 | 803 | 8 |
| $Co^{2+}$/PVDF | 1642 | 41 | 0.29 | 1657 | 11 | 0.60 | 811 | 13 |
| $Fe^{3+}$/PVDF | 1643 | 37 | 0.17 | 1653 | 11 | 0.83 | 806 | 9 |
| $Cr^{3+}$/PVDF | 1642 | 21 | 0.95 | | | | 805 | 14 |
| PVDF | | | | | | | | |
| $KNO_3$ | | | | | | | 806 | 7 |
| DMF | | | | 1660 | 17 | | | |

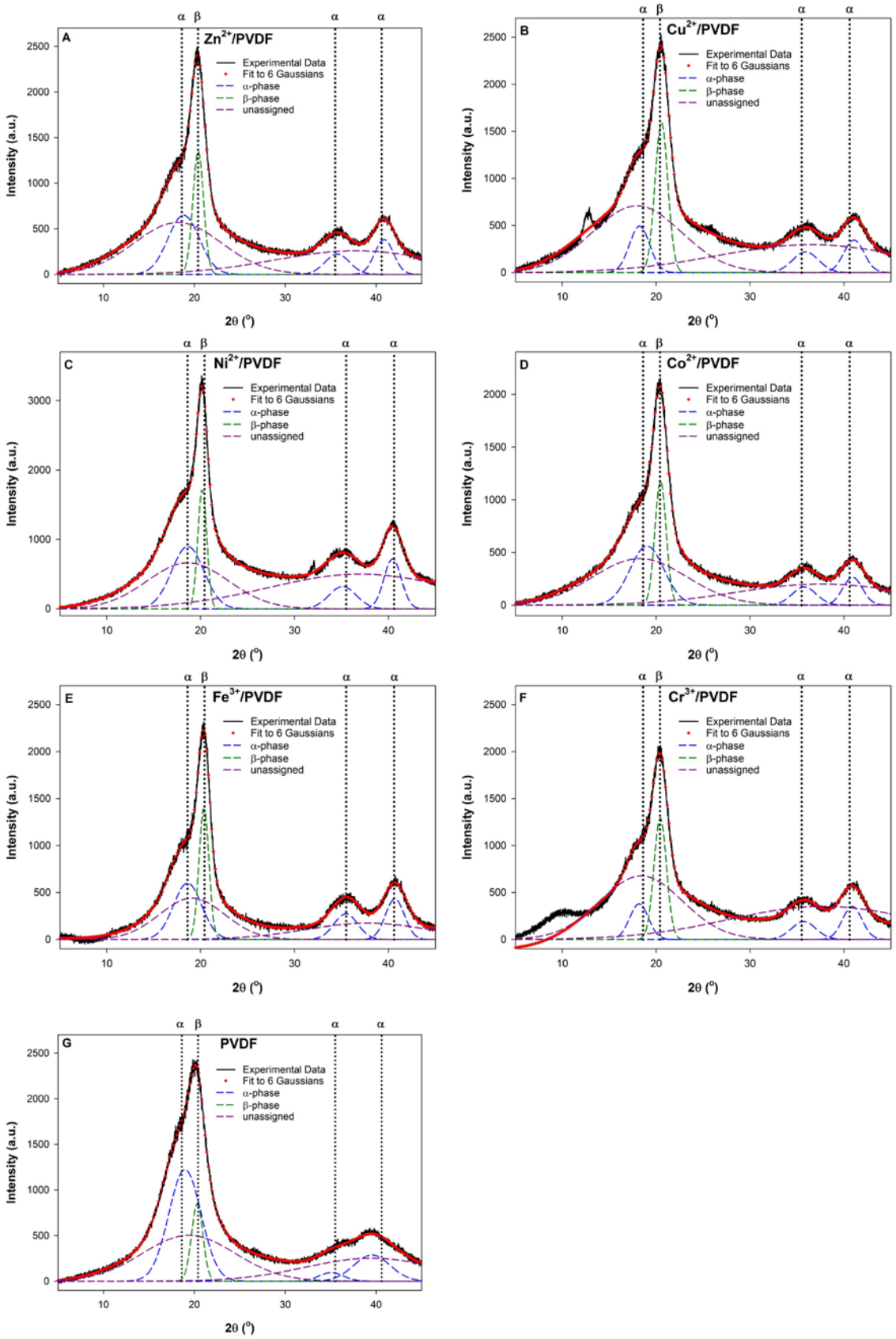


**Figure S2**. XRD data for doped/undoped PVDF films showing the deconvolutions. **A**: $Zn^{2+}$/PVDF. **B**: $Cu^{2+}$/PVDF. **C**: $Ni^{2+}$/PVDF. **D**: $Co^{2+}$/PVDF. **E**: $Fe^{3+}$/PVDF. **F**: $Cr^{3+}$/PVDF. **G**: PVDF.

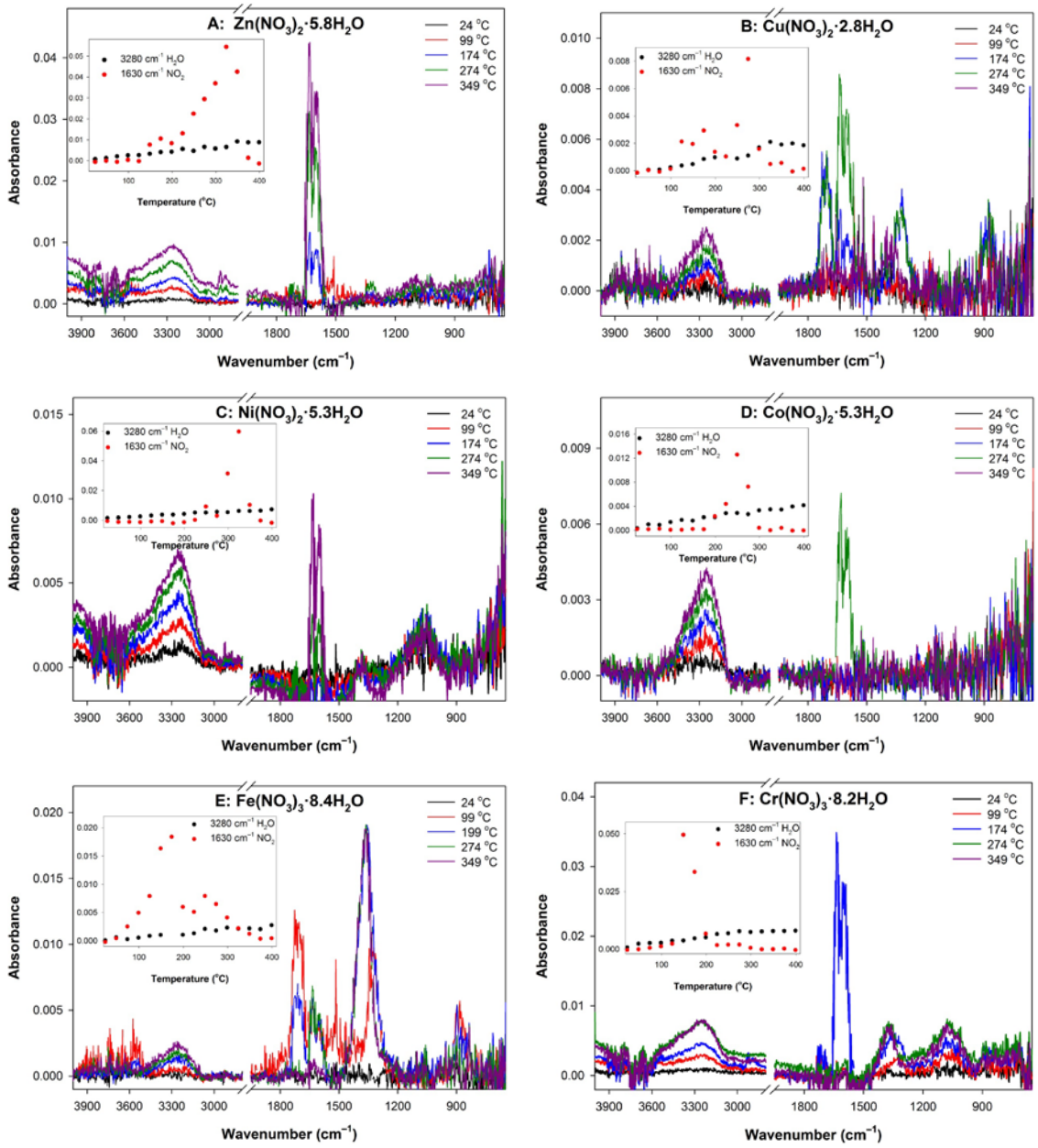


**Figure S3.** Gas phase IR spectra of the volatile products of the thermal decomposition of pure metal nitrate hydrates as a function of temperature. **A** $Zn(NO_3)_2{\cdot}5.8H_2O$; **B** $Cu(NO_3)_2{\cdot}2.8H_2O$; **C** $Ni(NO_3)_2{\cdot}5.3H_2O$; **D** $Co(NO_3)_2{\cdot}5.3H_2O$; **E** $Fe(NO_3)_3{\cdot}8.4H_2O$; **F** $Cr(NO_3)_3{\cdot}8.2H_2O$. The insets show the temperature dependence of the $H_2O$ (3280 $cm^{-1}$) and $NO_2$ (1630 $cm^{-1}$) peak intensities.

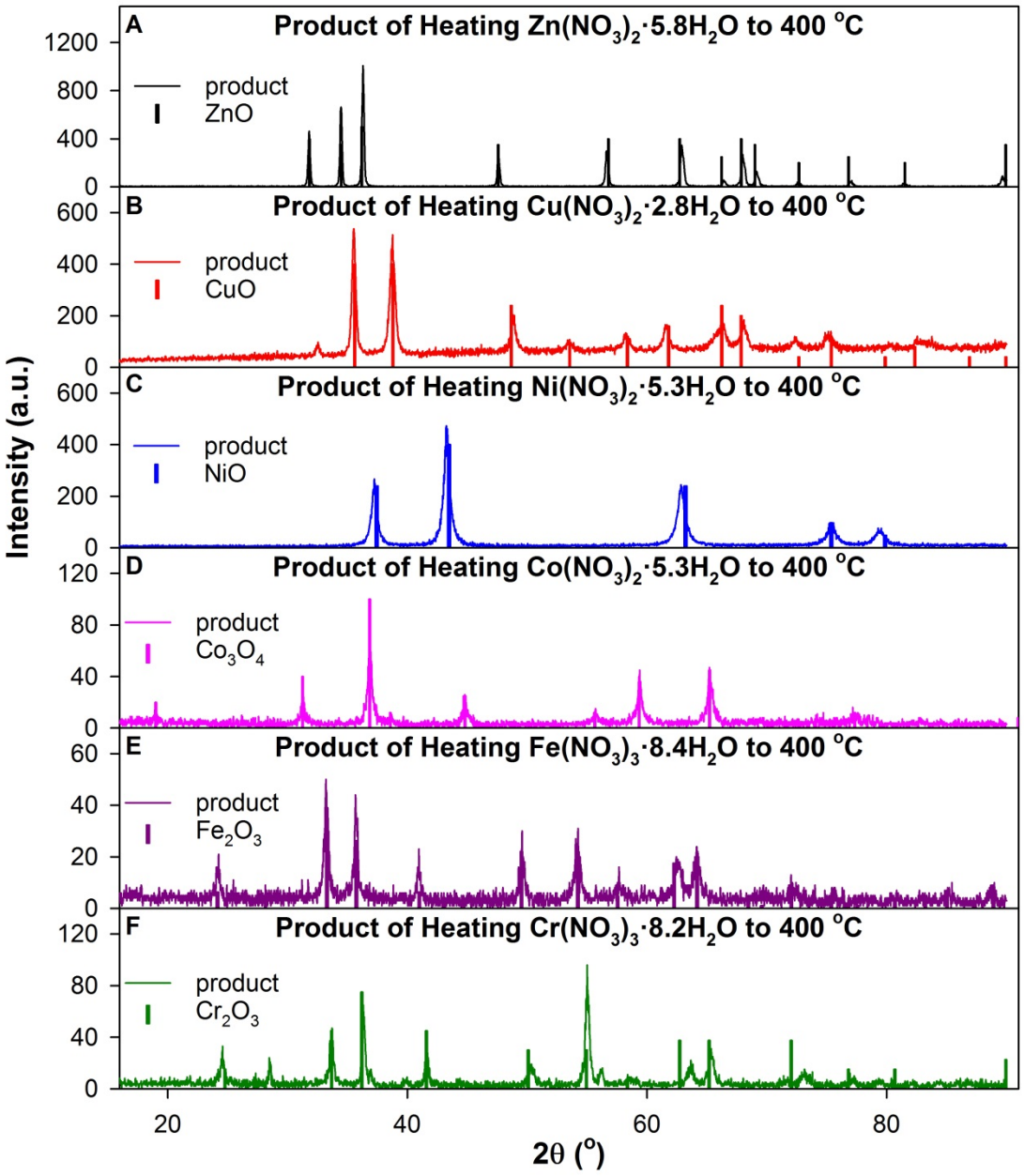


**Figure S4**. XRD results of metal nitrate hydrates heated to 400 °C. **A**: $Zn(NO_3)_2 \cdot 5.8H_2O$; **B**: $Cu(NO_3)_2 \cdot 2.8H_2O$; **C**: $Ni(NO_3)_2 \cdot 5.3H_2O$; **D**: $Co(NO_3)_2 \cdot 5.3H_2O$; **E**: $Fe(NO_3)_3 \cdot 8.4H_2O$; **F**: $Cr(NO_3)_3 \cdot 8.2H_2O$. The vertical bars show the literature reference values for the indicated oxides. The data for the oxides was taken from International Center for Diffraction Data (ICDD) reference library.

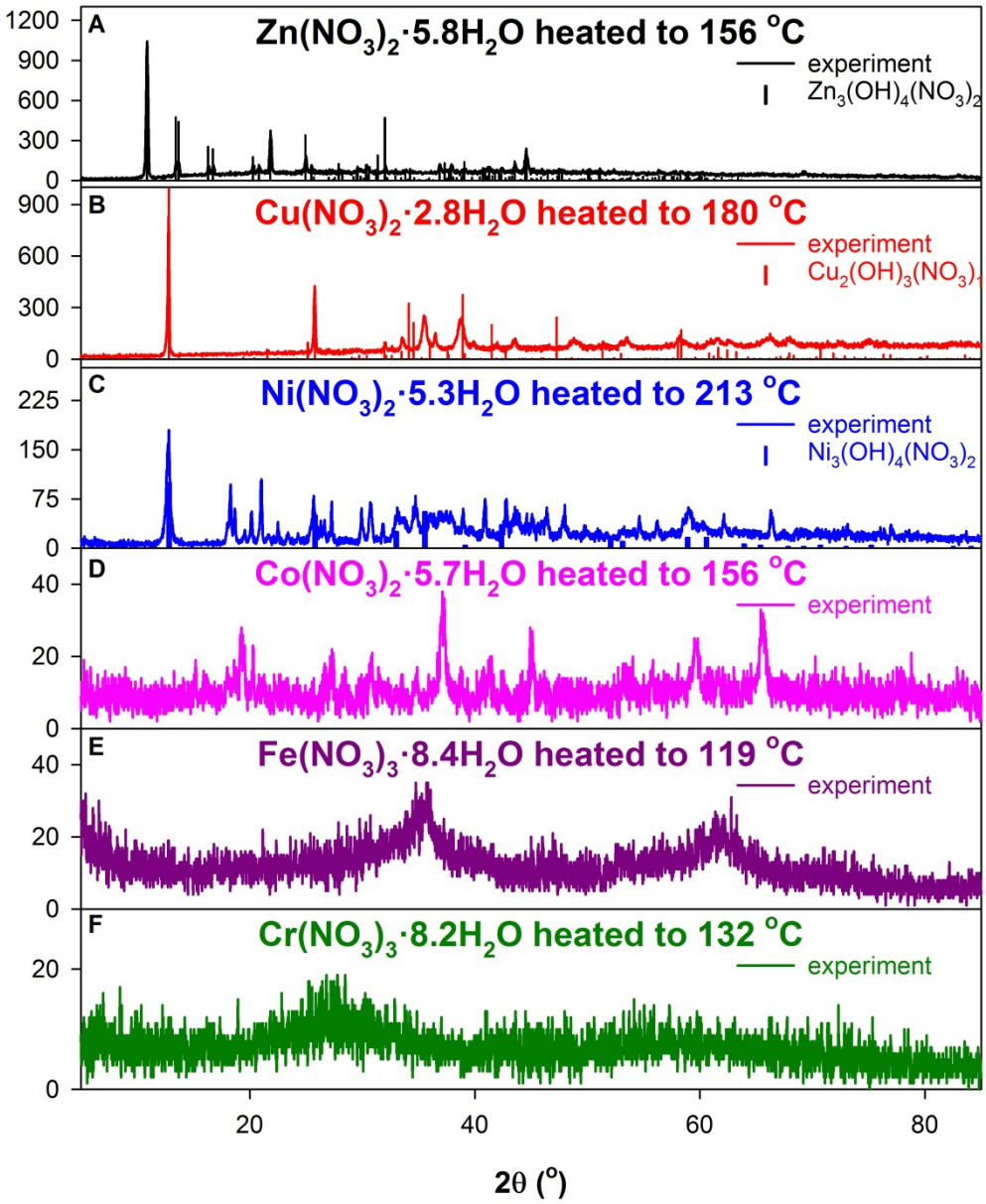


**Figure S5**. XRD results of metal nitrate hydrates heated to the onset temperature of the intermediate product. **A**: $Zn(NO_3)_2 \cdot 5.8H_2O$ heated to 156 °C; **B**: $Cu(NO_3)_2 \cdot 2.8H_2O$ heated to 180 °C; **C**: $Ni(NO_3)_2 \cdot 5.3H_2O$ heated to 213 °C; **D**: $Co(NO_3)_2 \cdot 5.3H_2O$ heated to 156 °C; **E**: $Fe(NO_3)_3 \cdot 8.4H_2O$ heated to 119 °C; **F**: $Cr(NO_3)_3 \cdot 8.2H_2O$ heated to 132 °C. The vertical bars show the literature reference values for the indicated hydroxide/nitrate double salts. The data for the double salts was taken from International Center for Diffraction Data (ICDD) reference library.

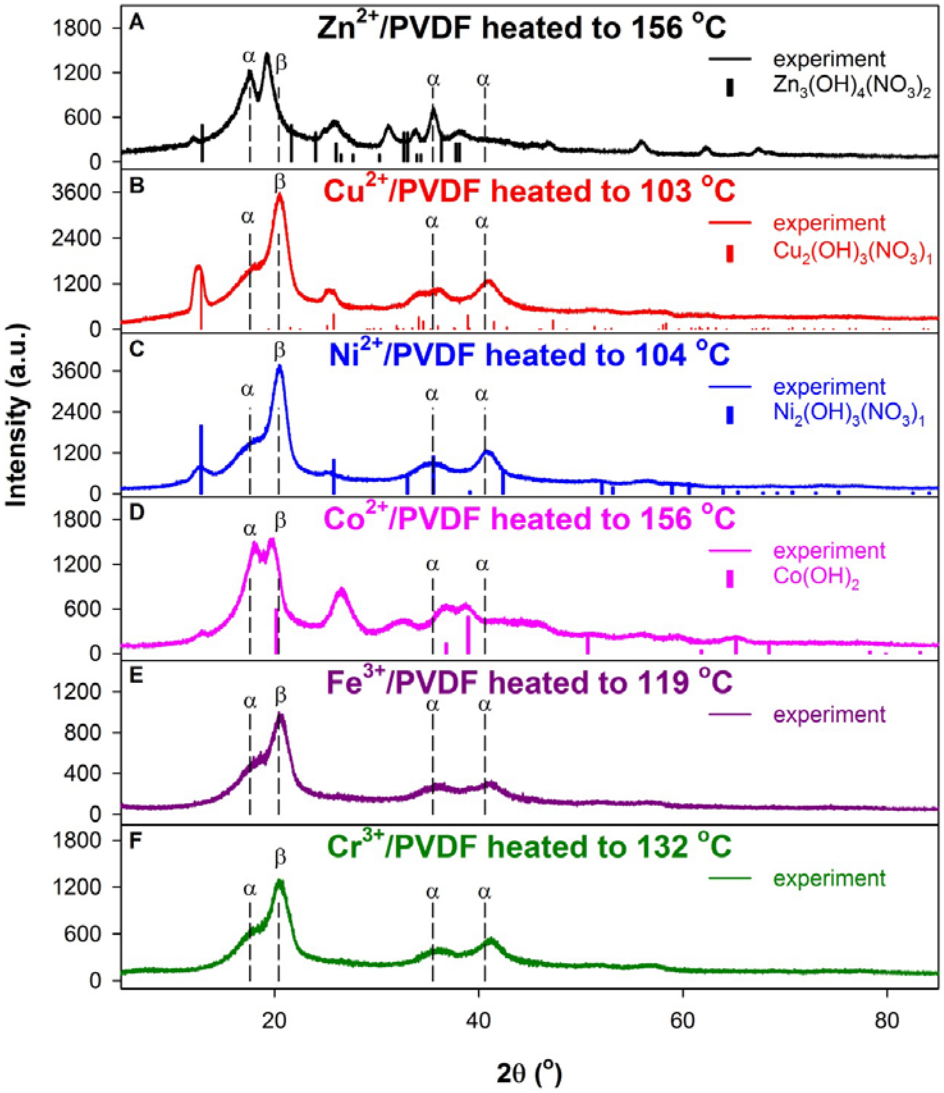


**Figure S6**. XRD results of doped PVDF heated to the onset temperature of the intermediate product. **A**: $Zn^{2+}$/PVDF heated to 156 °C; **B**: $Cu^{2+}$/PVDF heated to 103 °C; **C**: $Ni^{2+}$/PVDF heated to 104 °C; **D**: $Co^{2+}$/PVDF heated to 156 °C; **E**: $Fe^{3+}$/PVDF heated to 119 °C; **F**: $Cr^{3+}$/PVDF heated to 132 °C. The vertical bars show the literature reference values for the indicated hydroxide/nitrate salts. The data for the salts was taken from International Center for Diffraction Data (ICDD) reference library.

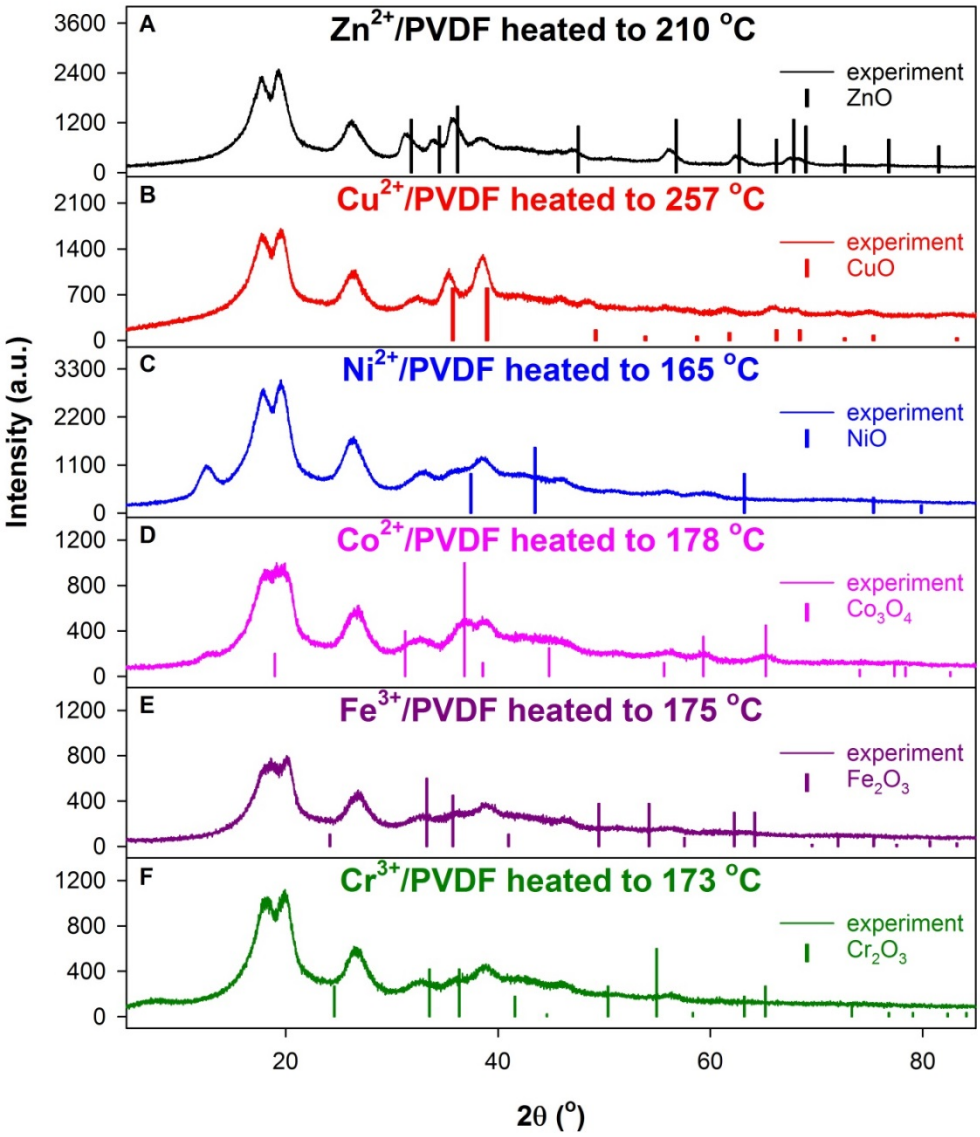


**Figure S7**. XRD results of doped PVDF heated to the onset temperature of the final product. **A**: $Zn^{2+}$/PVDF heated to 210 °C; **B**: $Cu^{2+}$/PVDF heated to 257 °C; **C**: $Ni^{2+}$/PVDF heated to 165 °C; **D**: $Co^{2+}$/PVDF heated to 178 °C; **E**: $Fe^{3+}$/PVDF heated to 175 °C; **F**: $Cr^{3+}$/PVDF heated to 173 °C. The vertical bars show the literature reference values for the indicated oxides. The data for the oxides was taken from International Center for Diffraction Data (ICDD) reference library.

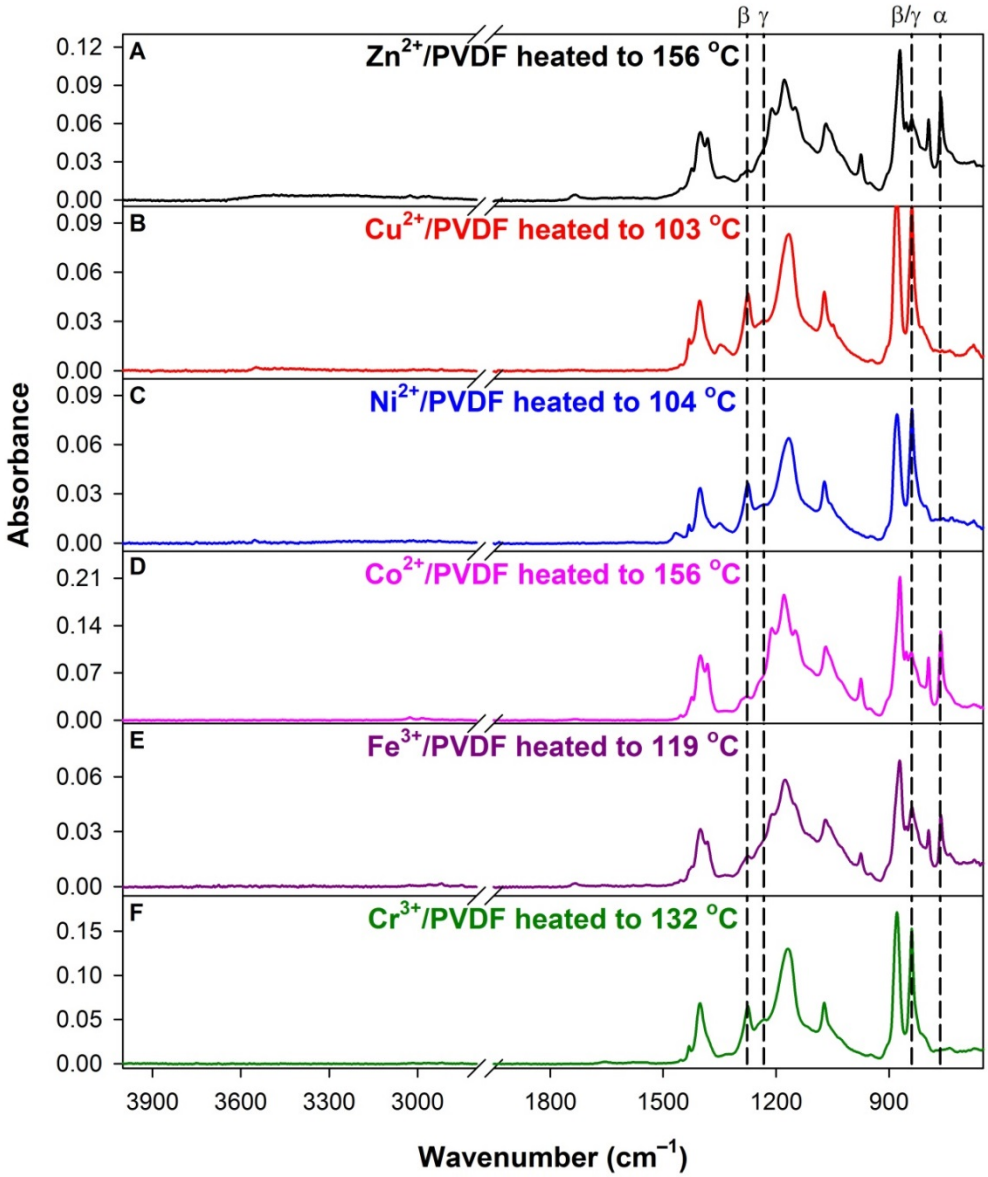


**Figure S8**. FTIR results of doped PVDF heated to the onset temperature of the intermediate product. **A**: $Zn^{2+}$/PVDF heated to 156 °C; **B**: $Cu^{2+}$/PVDF heated to 103 °C; **C**: $Ni^{2+}$/PVDF heated to 104 °C; **D**: $Co^{2+}$/PVDF heated to 156 °C; **E**: $Fe^{3+}$/PVDF heated to 119 °C; **F**: $Cr^{3+}$/PVDF heated to 132 °C.

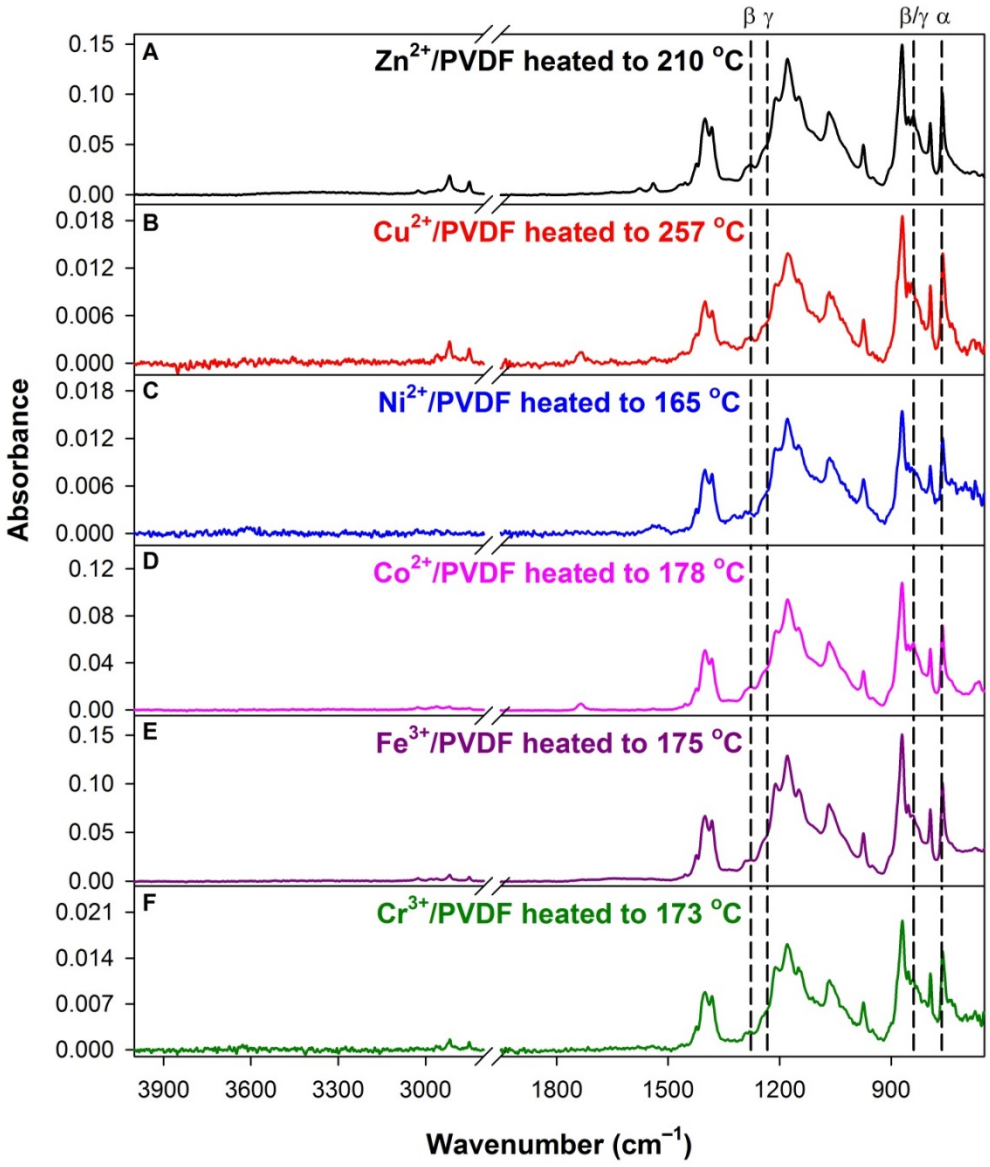


**Figure S9**. FTIR results of doped PVDF heated to the onset temperature of the final product. **A**: $Zn^{2+}$/PVDF heated to 210 °C; **B**: $Cu^{2+}$/PVDF heated to 257 °C; **C**: $Ni^{2+}$/PVDF heated to 165 °C; **D**: $Co^{2+}$/PVDF heated to 178 °C; **E**: $Fe^{3+}$/PVDF heated to 175 °C; **F**: $Cr^{3+}$/PVDF heated to 173 °C.