Electronic supplementary information (ESI) in the manuscript

Redox Reactions in Strontium Iron Phosphates: Synthesis, Structures, and Characterization of $Sr_9Fe(PO_4)_7$ and $Sr_9FeD(PO_4)_7$

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Table S1a. Anisotropic Atomic Displacement Parameters in $Sr_9Fe(PO_4)_7$ at 293 K

Site	10^2U_{11} (Å^2)	10^2U_{22} (Å^2)	10^2U_{33} (Å^2)	10^2U_{12} (Å^2)	10^2U_{13} (Å^2)	10^2U_{23} (Å^2)
P1 [a]	0.6(5)	4.6(9)	3.6(8)	0.0	0.0	0.0
O12 [a]	4.3(5)	7.7(5)	12.7(6)	0.0	0.0	–9.3(9)

[a] The anisotropic Debye-Waller factor is computed as

$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

Table S1b. Anisotropic Atomic Displacement Parameters in $Sr_9FeD(PO_4)_7$ at 293 K

Site	10^2U_{11} (Å^2)	10^2U_{22} (Å^2)	10^2U_{33} (Å^2)	10^2U_{12} (Å^2)	10^2U_{13} (Å^2)	10^2U_{23} (Å^2)
Sr1	0.79(5)	$= U_{11}$	0.71(8)	0.15(6)	–0.15(3)	$= -U_{13}$
Fe5	0.37(8)	$= U_{11}$	0.30(13)	$= 0.5U_{11}$	0	0
P2	1.24(8)	$= U_{11}$	0.68(10)	1.08(9)	–0.07(4)	$= -U_{13}$
O11	7.0(5)	$= U_{11}$	6.6(8)	$= 0.5U_{11}$	0	0
O21	3.09(10)	$= U_{11}$	0.33(9)	2.35(11)	–0.07(4)	$= -U_{13}$
O22	1.19(7)	0.76(6)	1.00(7)	–0.21(6)	–0.01(6)	–0.35(6)
O24	0.46(6)	$= U_{11}$	1.14(10)	0.20(7)	–0.00(4)	$= -U_{13}$

[a] The anisotropic Debye-Waller factor is computed as

$\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})]$.

Table S2. Fractional Coordinates and Atomic Displacement Parameters for $Sr_9FeD(PO_4)_7$ at 293 K Determined from the Synchrotron XRD Data

Site	Wyckoff position	*g*	*x*	*y*	*z*	10^2U (Å^2)
Sr1	18*h*	1	0.19258(3)	= –*x*	0.53705(3)	1.94(2)
Sr31	18*h*	1/3	–0.51167(14)	= –*x*	0.0057(2)	1.86(4)
Sr32	18*h*	1/6	–0.5325(3)	= –*x*	0.0115(3)	= *U*(Sr31)
Fe	3*a*	1	0	0	0	0.28(4)
P1	6*c*	1/2	0	0	0.5059(9)	2.4(2)
P2	18*h*	1	0.49238(6)	= –*x*	0.39651(8)	0.56(3)
O11	6*c*	1/2	0	0	0.5828(9)	9.2(6)
O12	36*i*	1/4	0.9691(9)	0.1125(7)	0.5221(4)	1.8(3)
O21	18*h*	1	0.53318(14)	= –*x*	0.67673(13)	0.72(8)
O22	36*i*	1	0.2671(2)	0.0152(2)	0.23516(11)	0.83(5)
O24	18*h*	1	0.91052(11)	= –*x*	0.06799(13)	0.16(7)

FIG. S1. The isothermal magnetization curves, M vs H, at 1.8 K for $Sr_9FeD(PO_4)_7$ oxidized at different temperatures.

FIG. S2. C_p vs T and C_p/T vs T curves for $Sr_9Fe(PO_4)_7$ between 0.4 and 55 K.

FIG. S3. Details of the IR and Raman spectra of $Sr_9Fe(PO_4)_7$ and $Sr_9FeD(PO_4)_7$.

FIG. S4. Mössbauer spectra of $Sr_9FeH(PO_4)_7$ and $Sr_9Fe(PO_4)_7$.

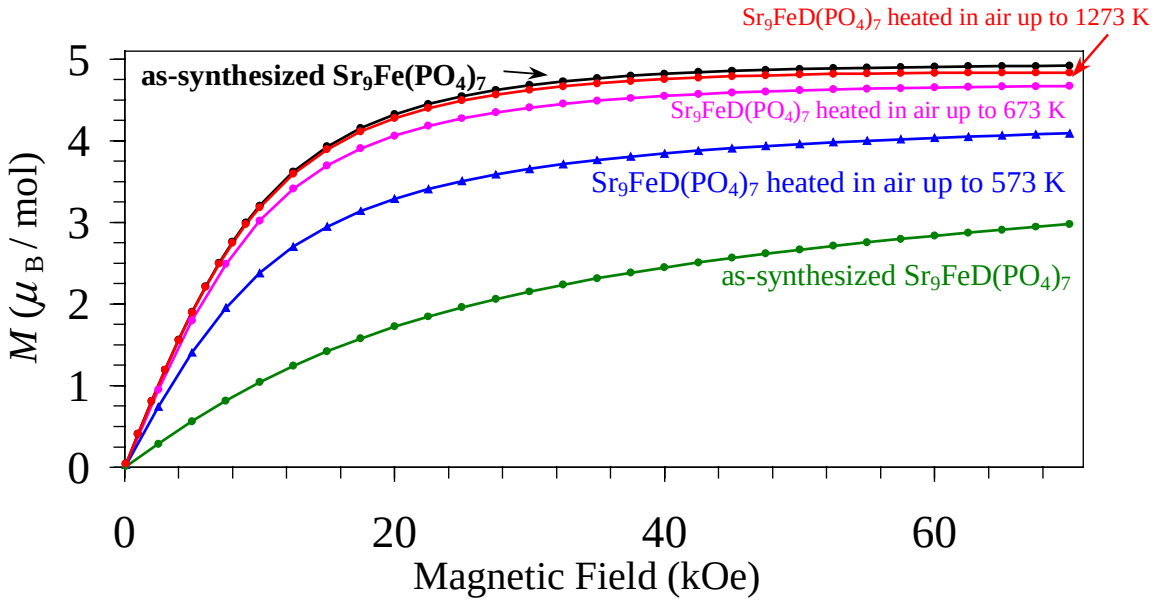


Figure S1

The isothermal magnetization curves, *M* vs *H*, at 1.8 K for the as-synthesized $Sr_9Fe(PO_4)_7$ and $Sr_9FeD(PO_4)_7$, and $Sr_9FeD(PO_4)_7$ heated in air at different temperatures.

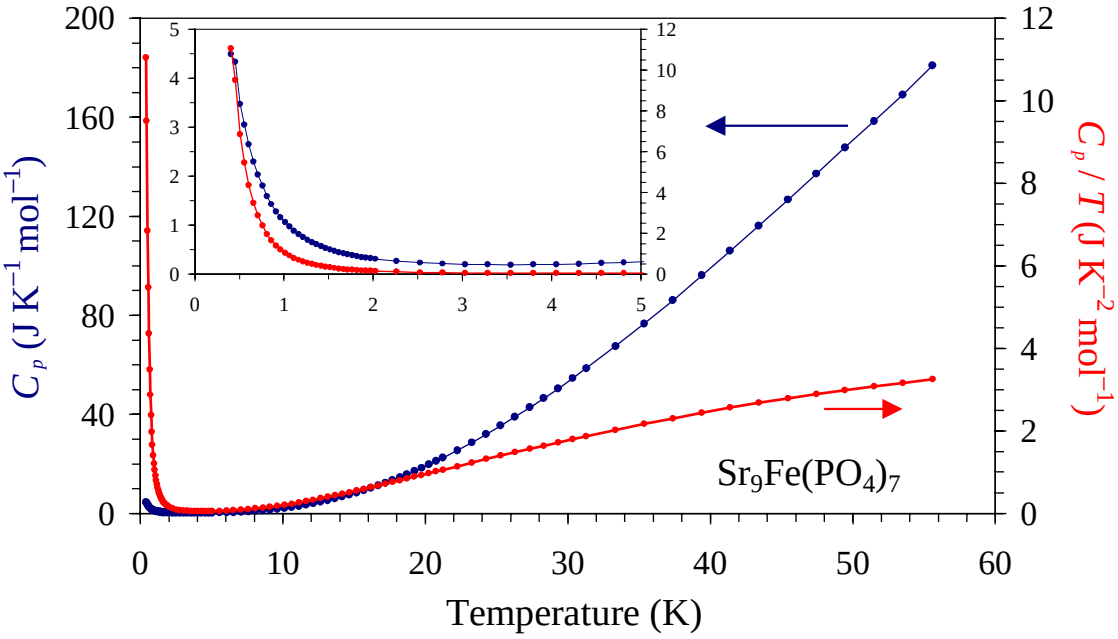


Figure S2

C_p vs T and C_p/T vs T curves for $Sr_9Fe(PO_4)_7$ between 0.4 and 55 K. The inset gives these curves between 0.4 and 5 K.

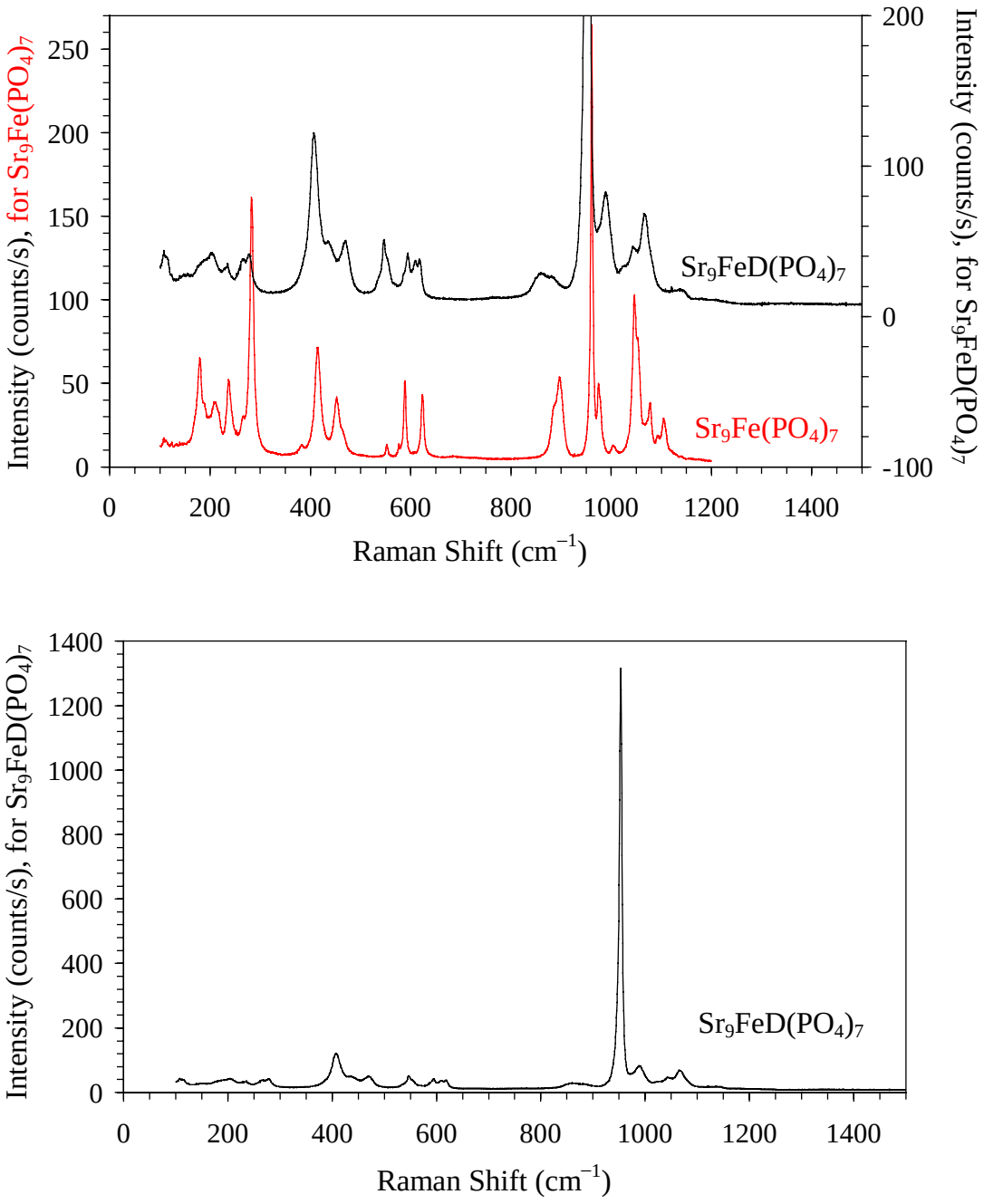


Figure S3a

Raman spectra of $Sr_9Fe(PO_4)_7$ and $Sr_9FeD(PO_4)_7$.

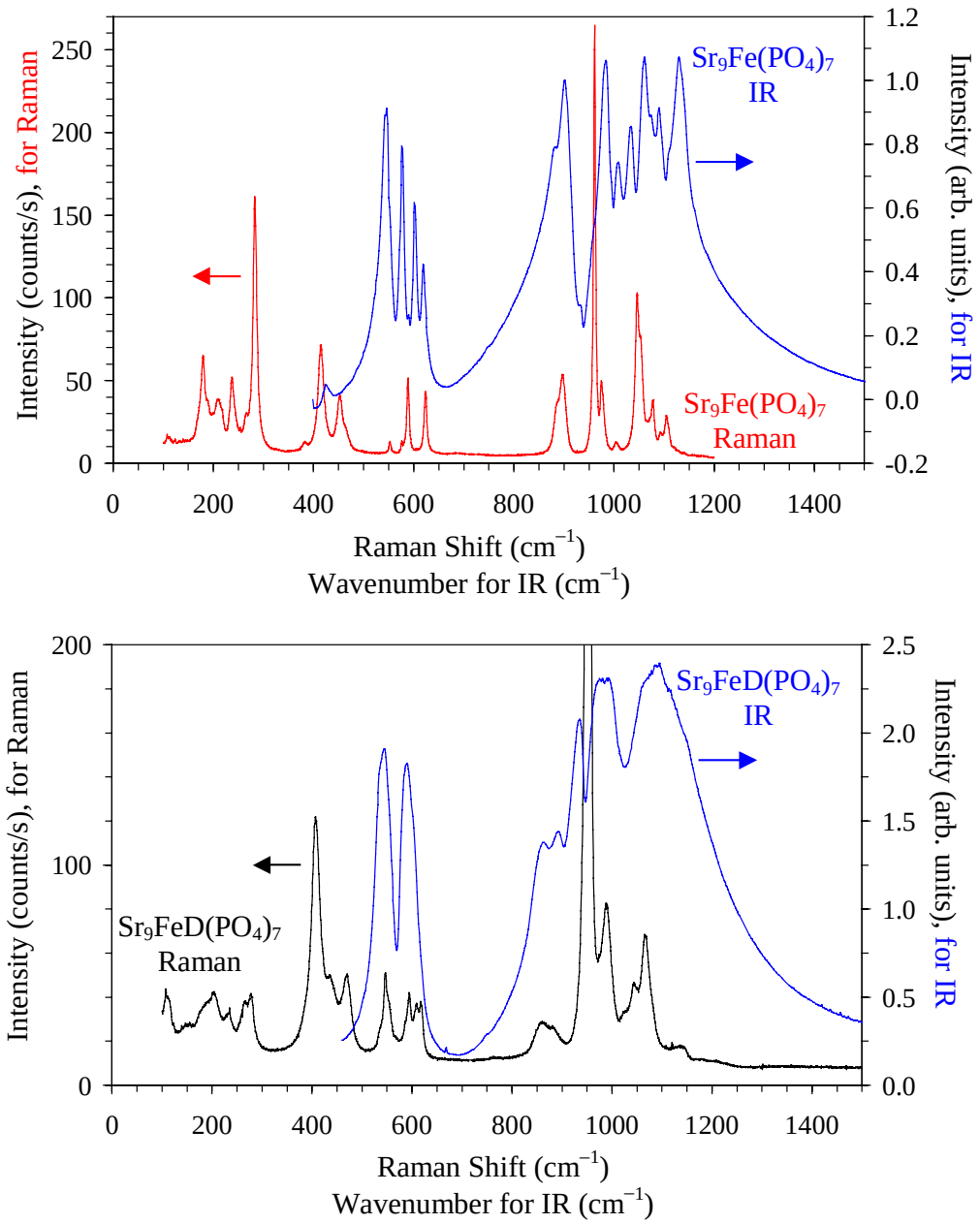
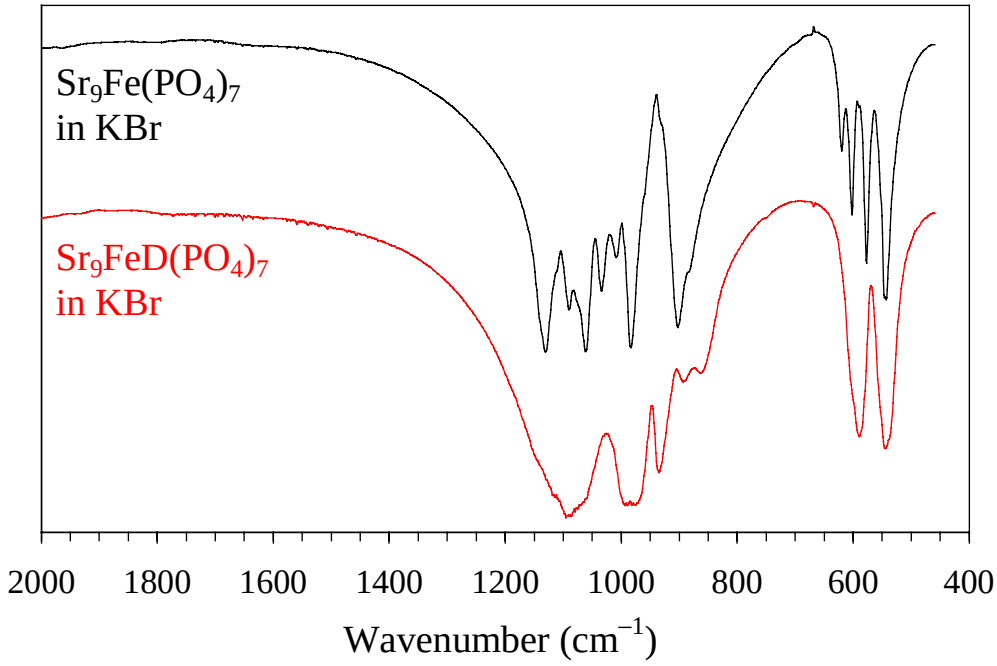


Figure S3b

Details of the IR and Raman spectra of $Sr_9Fe(PO_4)_7$ and $Sr_9FeD(PO_4)_7$.



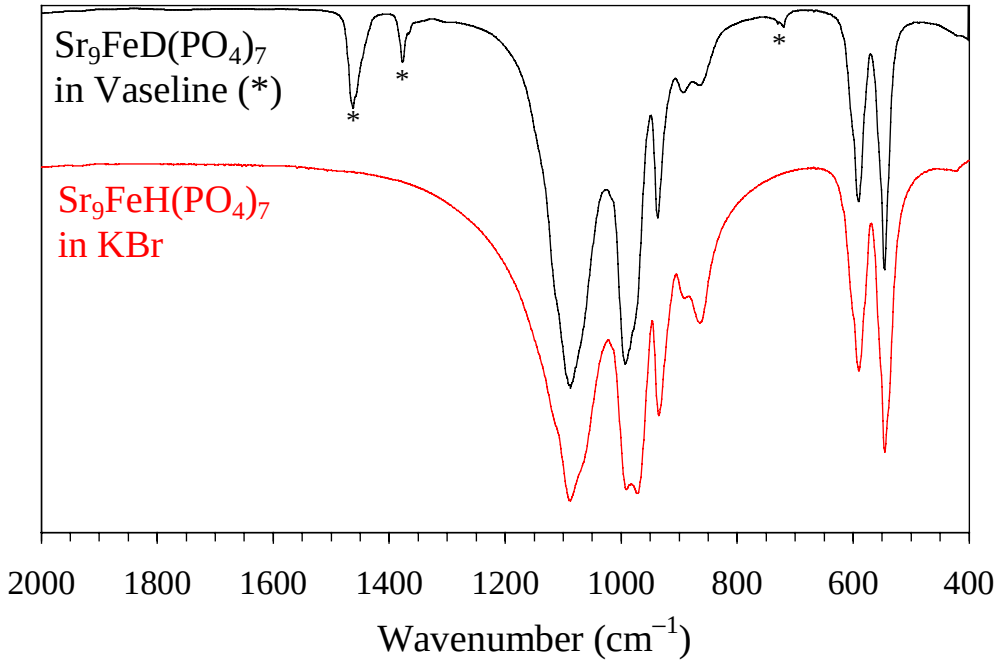


Figure S3c

Details of the IR spectra of $Sr_9Fe(PO_4)_7$, $Sr_9FeD(PO_4)_7$, and $Sr_9FeH(PO_4)_7$.

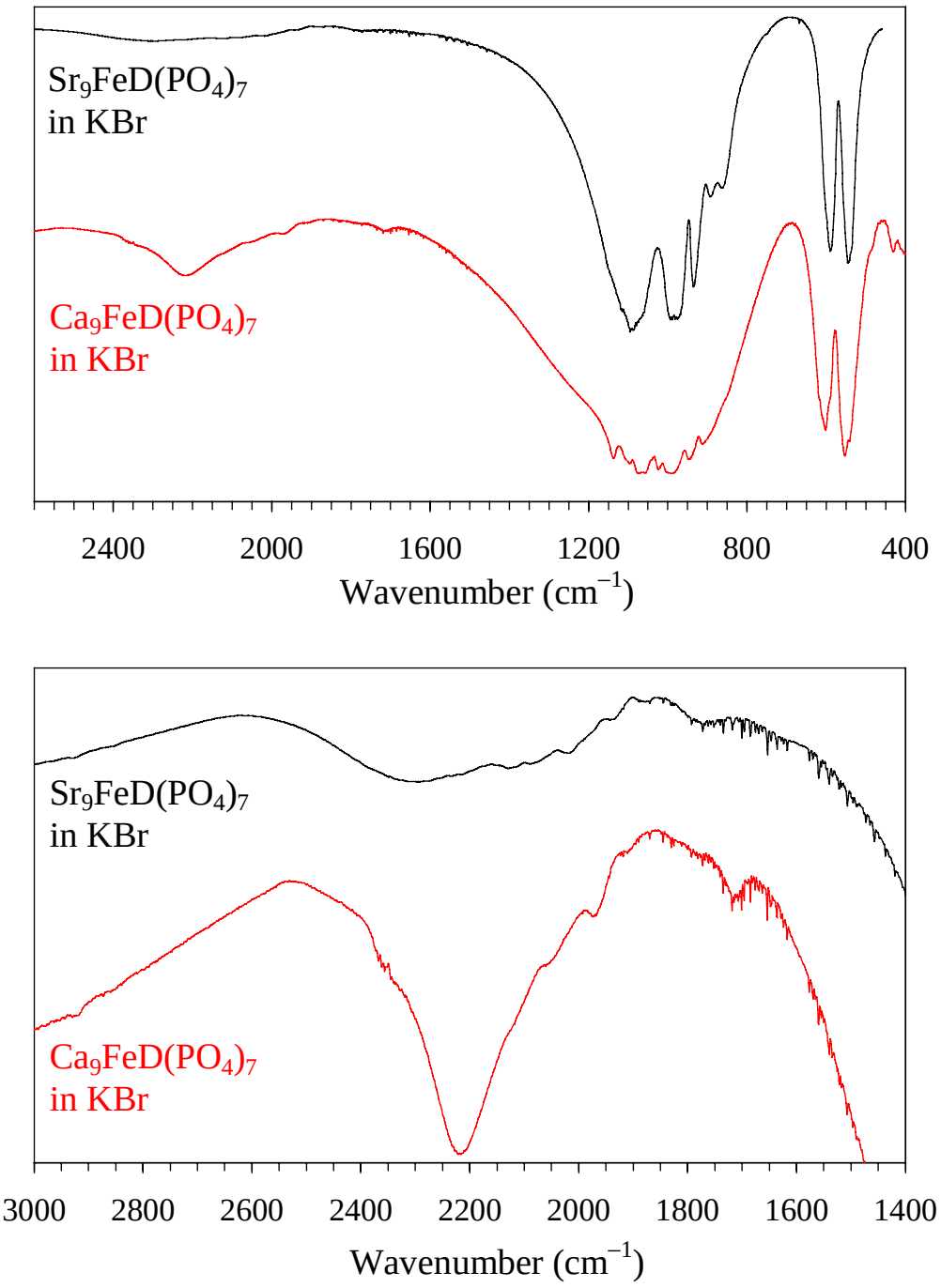


Figure S3d

The IR spectrum of $Sr_9FeD(PO_4)_7$ compared with that of $Ca_9FeD(PO_4)_7$.

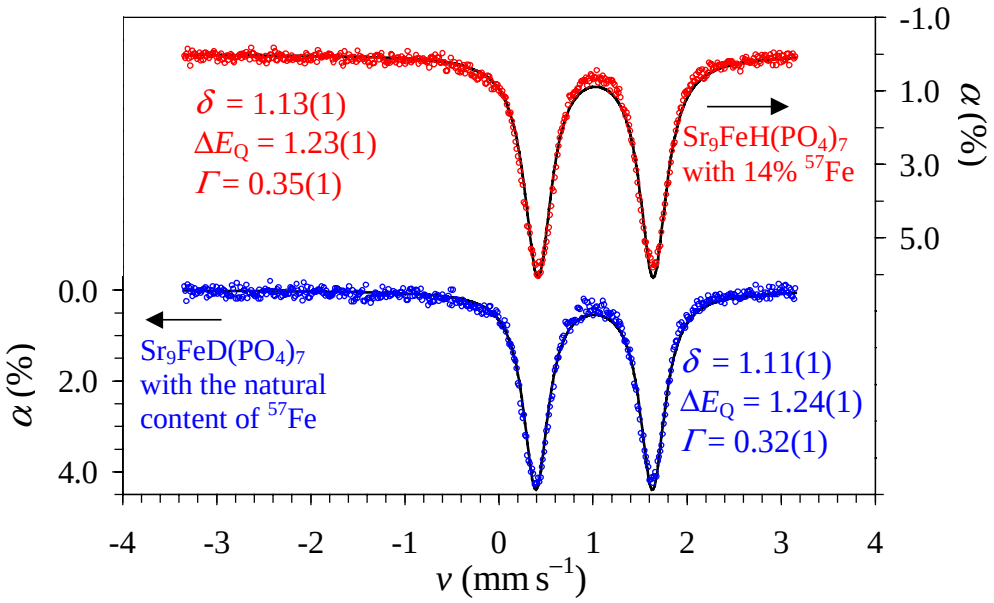


Figure S4a

Mössbauer spectrum of $Sr_9FeH(PO_4)_7$ at RT compared with that of $Sr_9FeD(PO_4)_7$.

v: velocity; α: absorption. Circles are experimental data, to which solid lines are fit. Hyperfine parameters refined by least-squares fitting are included in the figure, where δ is the isomer shift, ΔE_Q is the quadrupole splitting, and Γ is the full-width at half-maximum with a unit of mm s^{-1}.

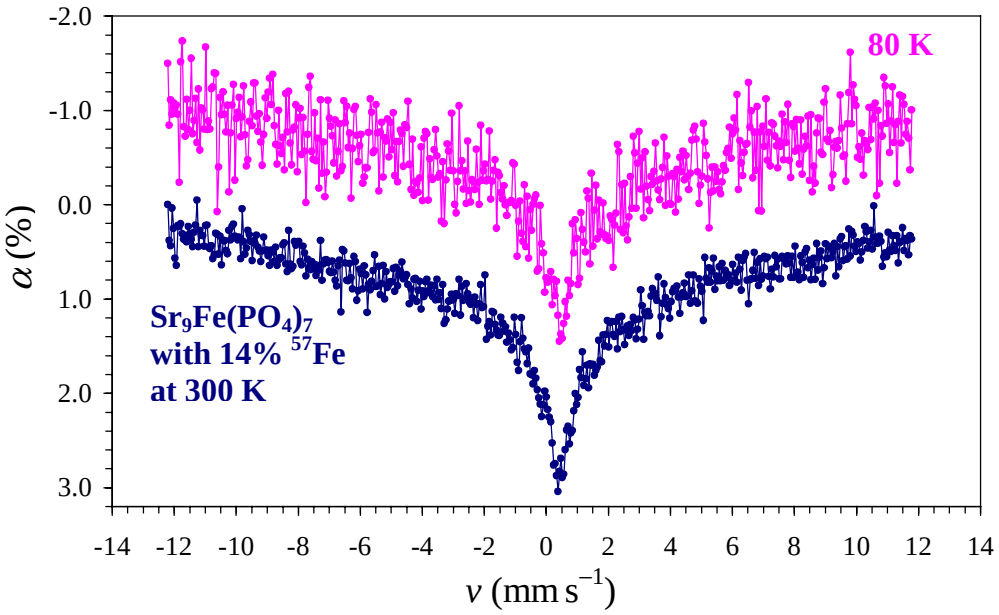


Figure S4b

Mössbauer spectra of $Sr_9Fe(PO_4)_7$ at 80 and 300 K. *v*: velocity; *α*: absorption. The spectrum at 80 K was shifted by –1.5 for the clarity.