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Supplementary Materials for

Interactions between alkali cations and cyanide-bridged network in $A_2Co_4[Fe(CN)_6]_{3.3}$ Prussian blue analogues revealed by far-infrared spectroscopy

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Figure S1. Far-IR spectra of CoFe PBAs of chemical formula $Cs_xCo_4[Fe(CN)_6]_{(8+x)/3}$•$nH_2O$ at 300 K over the 20-150 cm^{-1} frequency range, showing the variation of the band associated to the Cs^+ vibration mode with an increasing Cs^+ content x (and a decreasing amount of $Fe(CN)_6$ vacancies).

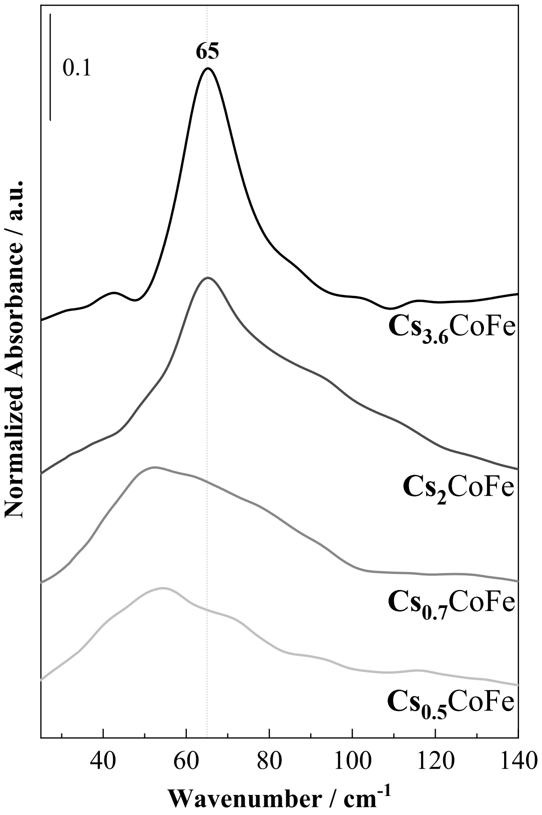


Figure S2. Far-Infrared spectra of **Na_2CoFe**, **Rb_2CoFe** and **Cs_2CoFe** recorded upon cooling.

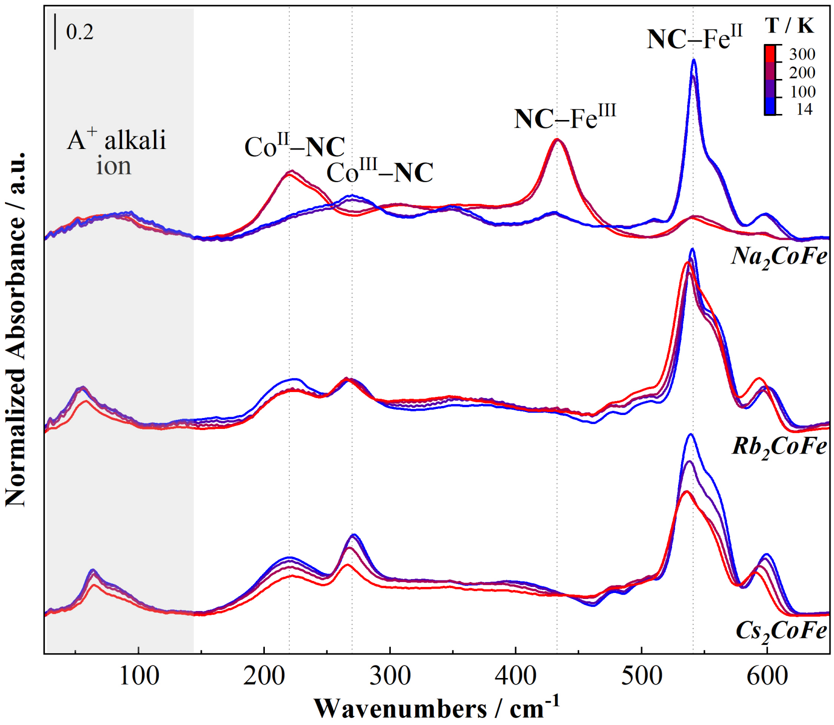


Figure S3. Far-Infrared spectra of **Rb_2CoFe** at 300K before cooling and after 1 and 2 cooling/heating cycles.

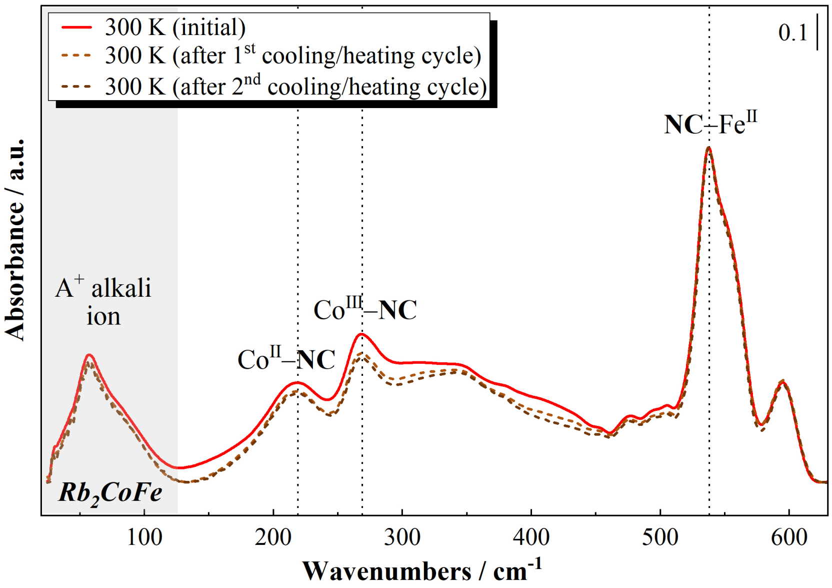
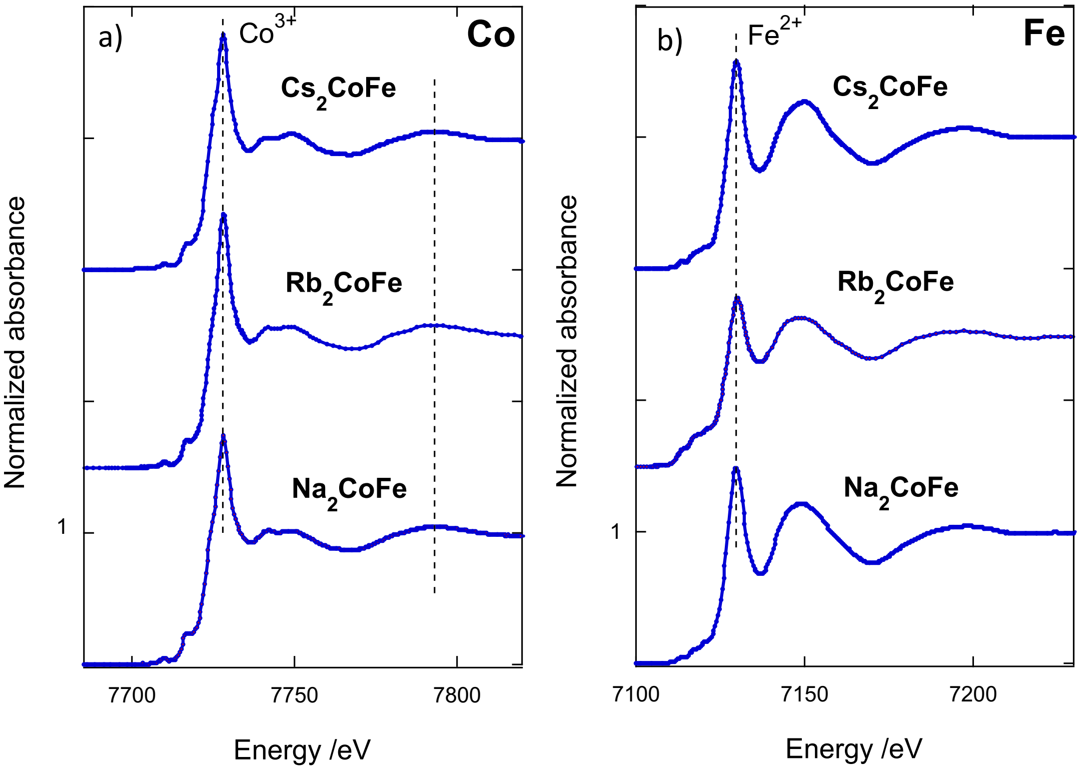
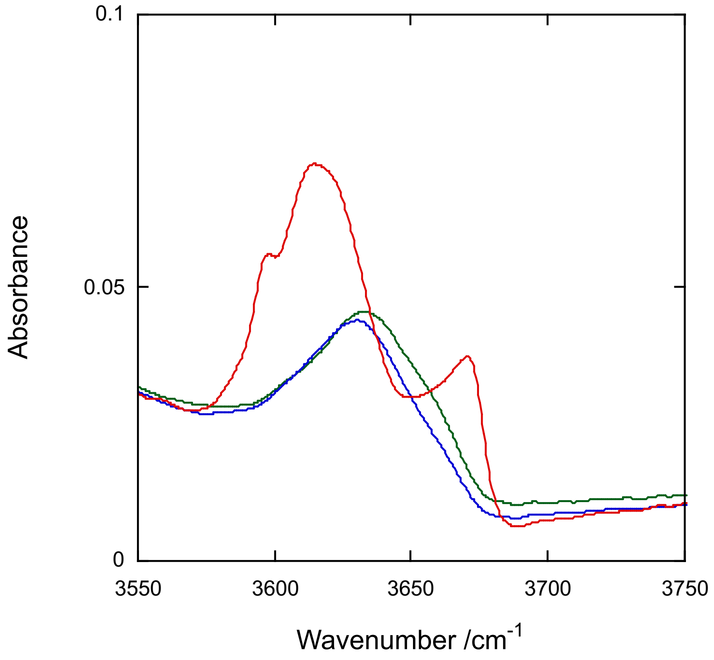


Figure S4. Low temperature X-ray Absorption Near Edge Spectra (XANES) of **Na_2CoFe**, **Rb_2CoFe** and **Cs_2CoFe** a) at the Co K-edge and b) at the Fe K-edge.



The shape of the spectra and the energy of the absorption maxima are characteristic of Co^{III} ions and $Fe^{II}(CN)_6$ entities in CoFe PBAs. The similarity of the spectra shows that all contain the same amount of these species, in line with the $Co^{II}_{0.7}Co^{III}_{3.3}[Fe^{II}(CN)_6]$ chemical formula.

Figure S5. Middle-Infrared spectra of **Na_2CoFe** (red), **Rb_2CoFe** (blue) and **Cs_2CoFe** (green) over the 3400-3800 cm^{-1} frequency range at 14 K.



The bands situated between 3500 and 3700 cm^{-1} correspond to stretching vibrations of OH bonds bound to the Co ions. The spectra of **Rb_2CoFe** and **Cs_2CoFe** are much different from the one of **Na_2CoFe**.

Table S1. Frequency of absorbance maximum, full-width at half maximum and area under peak for the three Gaussian components (*G1*, *G2*, *G3*).

	Na_2CoFe			**Rb_2CoFe**			**Cs_2CoFe**		
	G1	*G2*	*G3*	*G1*	*G2*	*G3*	*G1*	*G2*	*G3*
Frequency /cm^{-1}	541	558	600	539.5	559	601	536.5	557	600
Linewidth /cm^{-1}	12.7	24.6	23.2	16.2	23.6	22.8	20.2	27.9	22.3
Area /%	47	38.5	14.5	41	42	17	38	45	17