

Supporting Information

Two New Halide-Containing Cesium Manganese Vanadates: Synthesis, Characterization, and Magnetic Properties

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Summary of Supporting Information:

Figure S1. Calculated (a) and phase-pure (b) PXRD patterns for Cs₃Mn(VO₃)₄Cl (**I**).

Figure S2. Calculated (a) and phase-pure (b) PXRD patterns for Cs₂Mn(VO₃)₃F (**II**).

Figures S3-S4. EDX spectra displaying elemental composition in atomic percent for Cs₃Mn(VO₃)₄Cl (**I**) and Cs₂Mn(VO₃)₃F (**II**), respectively.

Raman Spectroscopy.

Figure S5. Raman spectra of Cs₃Mn(VO₃)₄Cl (**1**) and Cs₂Mn(VO₃)₃F (**2**) displayed from 300-1300cm⁻¹ with the polarization of the Raman beam indicated by arrows.

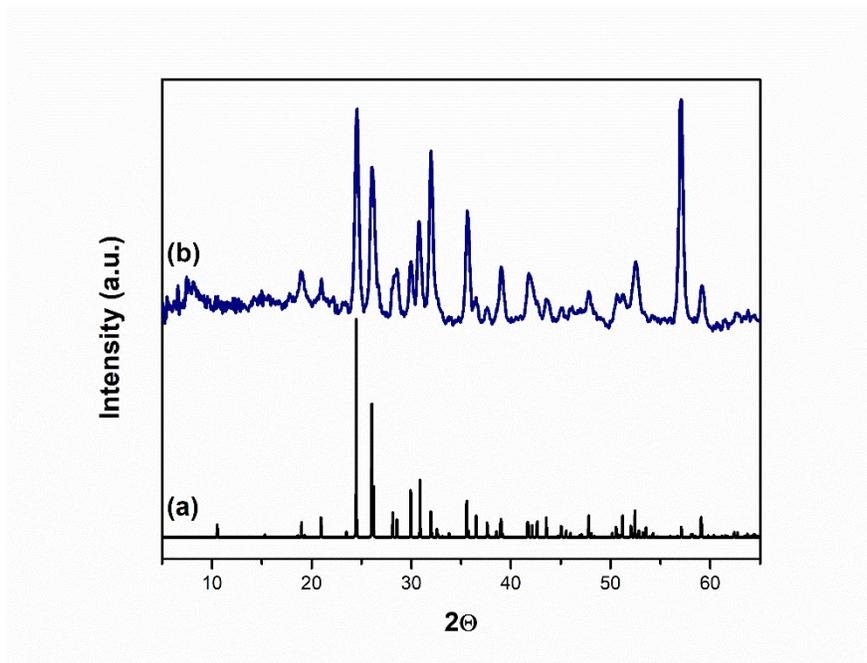


Figure S1. Calculated (a) and phase-pure (b) PXRD patterns for $\text{Cs}_3\text{Mn}(\text{VO}_3)_4\text{Cl}$ (**I**). Some preferred orientation effects are noted, due to the use of only a few individual crystal fragments for the PXRD measurement that was necessitated by the low yield of the halide-containing phase.

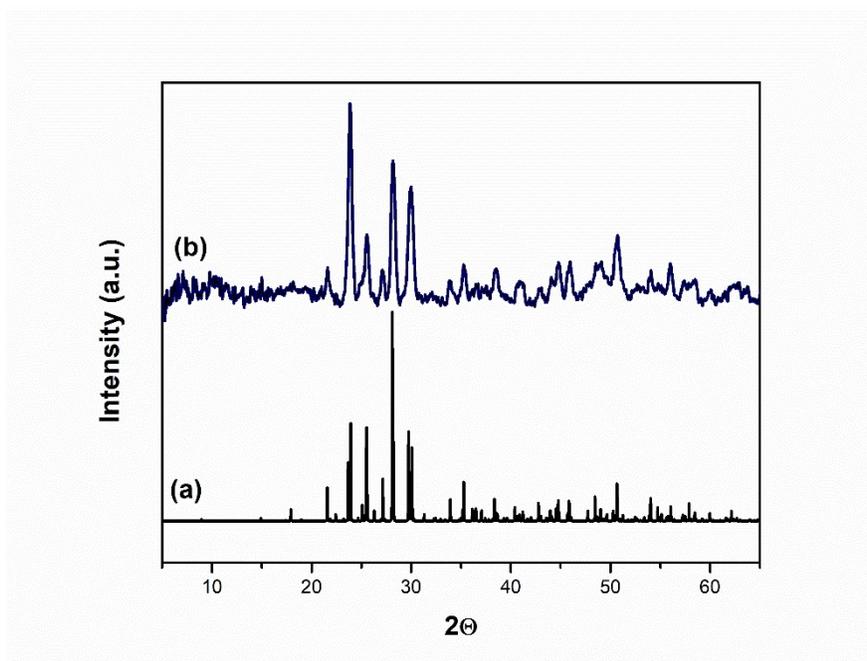


Figure S2. Calculated (a) and phase-pure (b) PXRD patterns for $\text{Cs}_2\text{Mn}(\text{VO}_3)_3\text{F}$ (**II**).

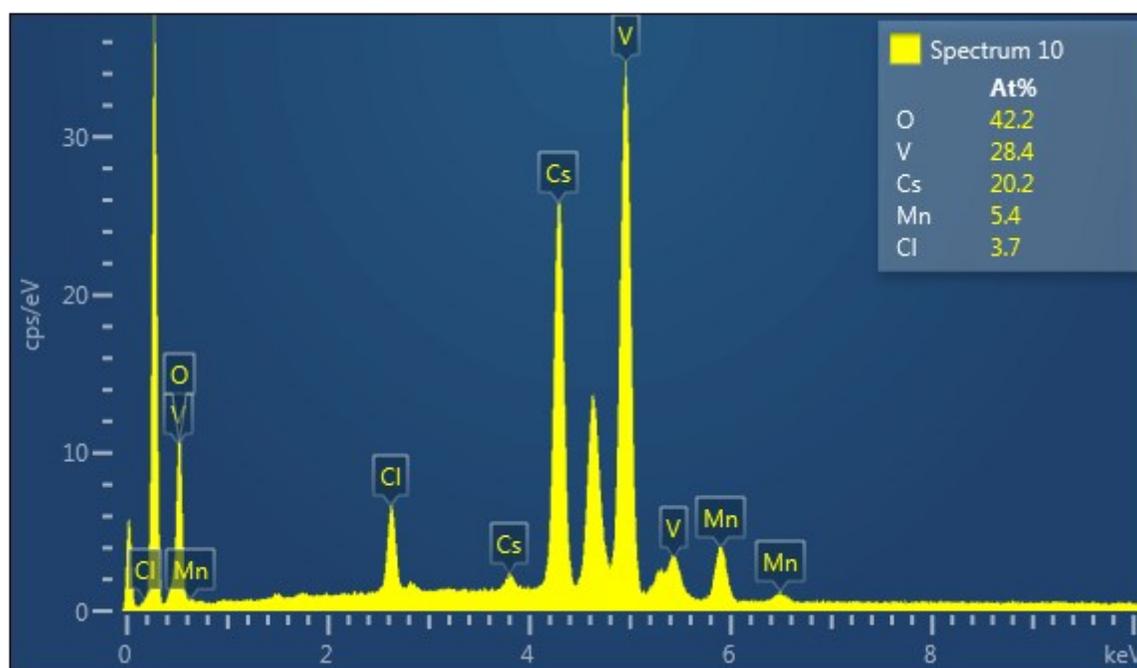


Figure S3. EDX spectra for $\text{Cs}_3\text{Mn}(\text{VO}_3)_4\text{Cl}$ (I) displaying elemental composition in atomic percent.

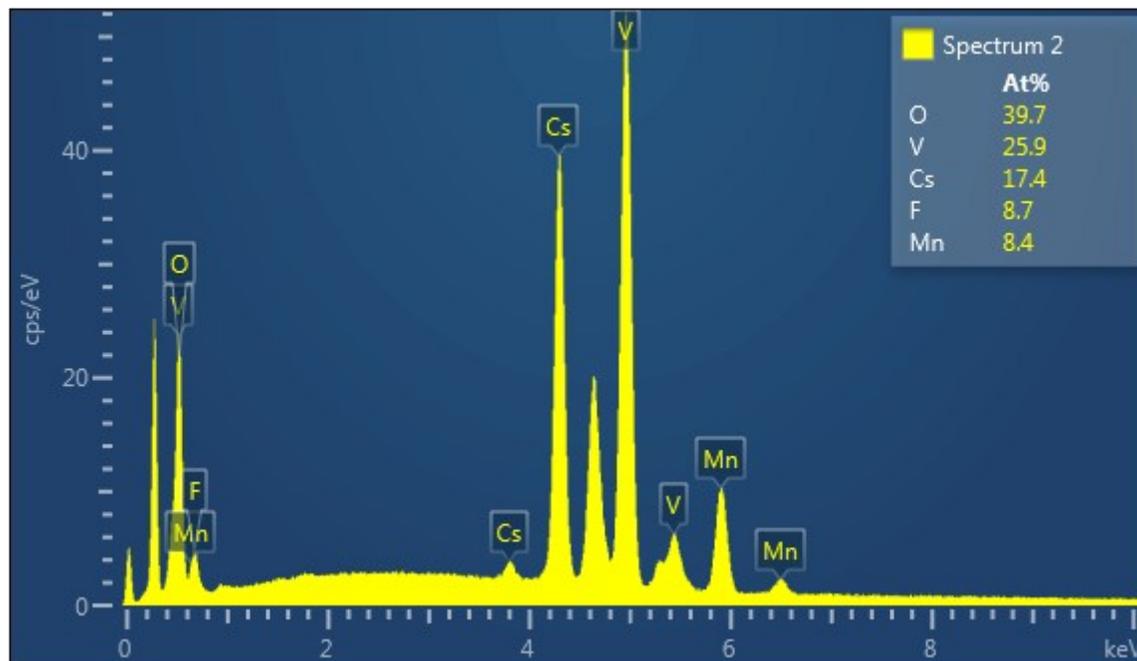


Figure S4. EDX spectra for $\text{Cs}_2\text{Mn}(\text{VO}_3)_3\text{F}$ (II) displaying elemental composition in atomic percent.

Raman Spectroscopy.

The single crystal Raman spectra of **1** and **2** are displayed in Figure S5. The Raman vibrational frequencies of vanadates are affected by several factors such as crystal symmetry and the presence of alkali, alkaline earth, and transitional metal ions, along with their respective oxidation states.¹⁻³ Due to these factors, there can be some ambiguity in the assignment of the Raman bands. Both compounds in this work have the same transition metal (albeit in different environments) in the same oxidation state (Mn^{2+}) and contain the same alkali metal. The compounds contain $[\text{VO}_4]$ tetrahedra condensed into $(\text{VO}_3)_n$ chains that differ slightly as described above. The $(\text{VO}_3)_n$ chains in **1** have a decided polarity through alignment of the apices of the $[\text{VO}_4]$ units, and have a sinusoidal shape. The $(\text{VO}_3)_n$ chains in **2** do not exhibit the same sinusoidal curvature, and are twisted, with metavanadate chains related by inversion symmetry throughout the unit cell.

The weak Raman bands around 308cm^{-1} and 355cm^{-1} can be attributed to ν_2 $(\text{VO}_4)^{3-}$ bending modes. The next bands, between 500cm^{-1} and 510cm^{-1} can be assigned to the ν_1 (VOV) stretching vibration, and the bands at $\sim 640\text{cm}^{-1}$ can be attributed to asymmetric V-O-V stretching. The final two peaks, the weak band $\sim 800\text{cm}^{-1}$ and the strong Raman band $\sim 950\text{cm}^{-1}$ can both be assigned to the V-O terminal stretching vibrations.^{1,3}

The change in polarization of the Raman beam can cause differences in the Raman spectra based on the space group of the compound.⁴ It is interesting to note that the strongest Raman band in compound **1** at $\sim 950\text{cm}^{-1}$ is a single peak, however, when the polarization of the Raman beam is rotated by 90° , an additional peak forms at $\sim 960\text{cm}^{-1}$. This band is due to V-O terminal stretching vibrations, so it is possible that the additional peak is a consequence of the two terminal V-O

bonds, which are non-equivalent relative to the polar axis of the crystal, and the combination of polarization and crystal orientation allows both Raman bands to be expressed.

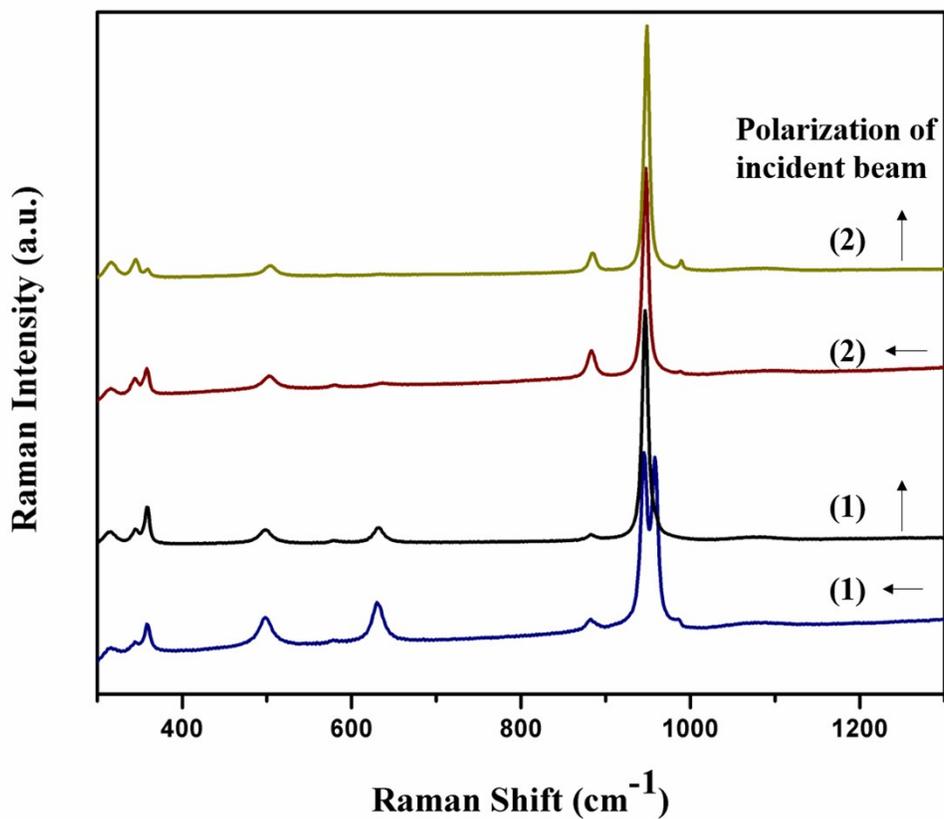


Figure S5. Raman spectra of $\text{Cs}_3\text{Mn}(\text{VO}_3)_4\text{Cl}$ (**1**) and $\text{Cs}_2\text{Mn}(\text{VO}_3)_3\text{F}$ (**2**) displayed from 300-1300 cm^{-1} with the polarization of the Raman beam indicated by arrows.

SI References:

- 1 T. Sivakumar, H. Y. Chang and P. S. Halasyamani, *Solid State Sci.*, 2007, **9**, 370–375.
- 2 Z. Luan, *J. Phys. Chem. B*, 1997, **101**, 9046–9051.
- 3 R. L. Frost, S. J. Palmer, J. Čejka, J. Sejkora, J. Plášil, S. Bahfenne and E. C. Keeffe, *J. Raman Spectrosc.*, 2011, **42**, 1701–1710.
- 4 D. Tuschel, *Spectroscopy*, 2014, **29**, 14–23.