Supplementary Information for

Direct Solvothermal Crystallisation of the Metastable Cubic Perovskite $CsMnF_3$ and its Magnetism

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Materials and Methods

MnF_2 (abcr GmbH, 98%). CsF (Merck, 99%) and ethylene glycol (ThermoFisher Scientific, 99.9%) were all used as received. For small-scale syntheses, 0.124 g MnF_2 (1.33 mmol, 1 equivalent) and 1.216 g CsF (8.01 mmol, 6 equivalents) were added to a Teflon-lined steel autoclave with an internal volume of 20 ml. To this, 10 ml ethylene glycol was added and the mixture was stirred for five minutes. The autoclave was then sealed and placed in a fan-assisted oven pre-heated to a temperature between 100 and 180 °C. The autoclave was then heated at this temperature for 72 hrs before being removed from the oven and allowed to cool to room temperature. The solid product was obtained by vacuum filtration, rinsed with 10 ml of fresh ethylene glycol and dried for 15 hours in a ventilated oven at 75 °C. The final product typically had a mass of ~0.15 g. All presented data except neutron powder diffraction data were collected from samples made using small-scale synthesis.

A large-scale sample was synthesised for a powder neutron diffraction experiment. The procedure was the same (reaction temperature 100 °C), with all reagent amounts and autoclave internal volume increased by a factor of 10. The large-scale sample was found to contain significantly more MnF_2 than the analogous small-scale reaction (see Results and Discussion).

Samples were initially assessed by laboratory X-ray powder diffraction (XRD) using a Panalytical Empyrean X-ray diffractometer using a Cu $K\alpha_{1,2}$ (λ = 1.54056 Å, 1.54439 Å) radiation in reflection (Bragg-Brentano) geometry. Two-phase (cubic $CsMnF_3$ and MnF_2) Rietveld fits were employed to obtain (crystalline) phase fractions. The instrument resolution and signal-to-noise were insufficient to see any 6H-$CsMnF_3$ present in the sample (further details below). It was noted that mild fluorescence of Mn in Cu Kα X-rays may introduce a systematic error, but no attempt to correct it was made in this preliminary analysis.

Synchrotron XRD data from the optimum sample was measured using beamline I11[1] (Diamond Light Source, UK) with λ = 0.826404(1) Å in transmission geometry. Samples were packed into capillaries in air. In a borosilicate capillary of diameter 0.2 mm, variable temperature from 300 K to 100 K were collected at a rate of 6 K min^{-1} using an Oxford Cryostream Plus. Variable temperature synchrotron XRD data were collected from a powder in a 0.2 mm quartz capillary whilst it was heated from room temperature up to 527 °C at a rate of 6 °C min^{-1} using a hot-air blower. Rietveld three-phase fits of cubic $CsMnF_3$, 6H-$CsMnF_3$ and MnF_2 were used (further details below).

Neutron powder diffraction data were collected using the high-flux diffractometer D1B[2] (Institut Laue-Langevin, France). 4 g of the large-scale sample was loaded into a cylindrical vanadium can (outer diameter 8 mm) which was placed into an "Orange" cryostat. The sample was then cooled to 10 K. A neutron diffraction pattern was collected for 10 minutes whilst the sample was held at 10 K using a Ge(113) monochromator with a take off angle of 44.22° (neutron λ = 1.28 Å). The neutron monochromator was then changed to highly-ordered pyrolytic graphite (002) (giving a neutron λ = 2.52 Å and extremely high flux) and diffraction data were collected in 1 minute accumulations from the sample as it was warmed at a rate of 1 K min^{-1} until the temperature reached 80 K (*n.b.* after the experiment, to improve signal to noise, the data were summed in three minute bins for further analysis). Another diffraction pattern was collected at 80 K using the λ = 1.28 Å neutron beam. In all measurements on D1B, the data do not detect any 6H-$CsMnF_3$, but a significant MnF_2 impurity is

apparent, and therefore two-phase Rietveld fits were utilised. The magnetic structure for cubic $CsMnF_3$ was determined from neutron powder data collected at 10 K using $\lambda = 1.28$ Å. The published[3] magnetic structure and temperature response of the MnF_2 yields a good fit to the observed MnF_2 magnetic peaks.

XRD and neutron powder diffraction data were analysed by the Rietveld method using the software Topas Academic v7.[4] In all cases, a background term, lattice parameters, scale factors and peak shape parameters were refined. All site occupancies were fixed at unity. For data collected to high Q (*i.e.* synchrotron XRD and neutron powder diffraction collected using a neutron wavelength of 1.28 Å) isotropic atomic displacement parameters (ADPs) and atomic coordinates were refined. For laboratory XRD, the ADPs and atomic coordinates were fixed at literature values.

Variable temperature synchrotron XRD and variable temperature neutron powder diffraction data were fitted against using a sequential method using the same starting model for each pattern. Limits (minimum and maximum values) were placed on peak shape parameters, lattice parameters and zero error to maintain sensible values. To minimise refined parameters in sequential fits, ADPs were constrained for a single value for each element across all phases (*i.e.* each refinement contained one Cs ADP, one Mn ADP and one F ADP).

Magnetometry measurements were performed on a Quantum Design MPMS-5S SQUID magnetometer. Around 20 mg of accurately weighed powdered sample was loaded into a gel capsule, encased within a plastic straw. Zero-field cooled (ZFC) and field cooled (FC) DC magnetic susceptibility, χ, measurements were taken in the range of 2–400 K with an applied field of 1000 Oe. A fit[5] was carried out against the paramagnetic region (350 – 400 K) of the inverse molar susceptibility using the Curie-Weiss law:

$$\chi_{\text{mol}}^{-1} = \frac{T - \theta_{\text{CW}}}{C}$$

where θ_{CW} is the Curie-Weiss temperature and C is the Curie constant. The effective moment, μ_{eff} is calculated in units of Bohr magnetons, μ_{B}, by:

$$\mu_{\text{eff}} = \sqrt{8C}\,\mu_{\text{B}}$$

Close to T_{N}, the variation of the Mn moment in $CsMnF_3$, μ(Mn), (refined from variable temperature neutron diffraction) as a function of temperature was fitted using a phenomenological critical power law[6]:

$$\mu = \mu_0\left(1 - \frac{T}{T_N}\right)^{\beta}$$

where μ_0 is the moment at $T = 0$ K, T_{N} is the Néel temperature and β is the critical exponent. It was necessary to fix μ_0 to 5 μ_0 to obtain a physical value. Fitting the full antiferromagnetic region (10 – 64 K) and allowing μ_0 to refine does not significantly affect the resulting values of T_{N} or β (Figure S3).

A ZEISS Gemini SEM-Field Emission Scanning Electron Microscope was used to collect scanning electron micrographs, using an accelerating voltage of 2 kV and a working distance of ~5.5 mm, with an Inlens Duo detector.

Supplementary Data

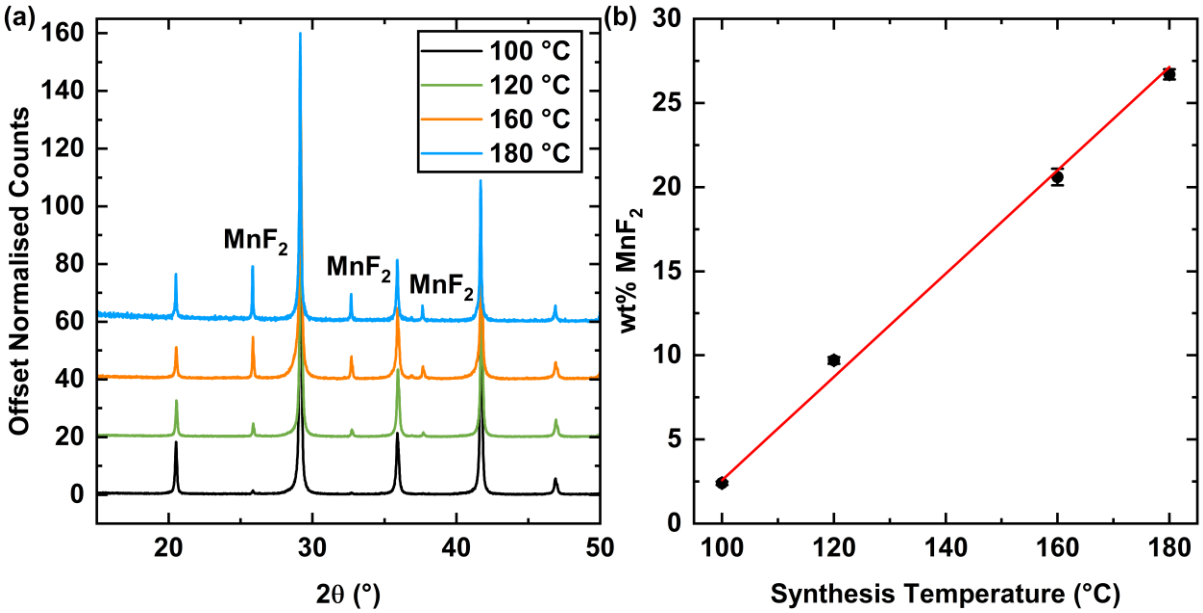

Figure S1. (a) Laboratory PXRD patterns (Cu Kα, $\lambda_{av.}$ = 1.5418 Å) of products made at synthesis temperatures between 100 °C and 180 °C. (b) the mass of MnF_2 found in the products by refinement against PXRD data. A fit (R = 0.995) in red highlights the linear relationship.

Table S1. Structural parameters from cubic $CsMnF_3$ ($Pm\bar{3}m$) refined using synchrotron XRD (I11) at 100 K and 300 K.

	100 K	**300 K**
***a*, Å**	4.316763(7)	4.330579(9)
***V*/ Å^3**	80.4405(4)	81.2153(5)
Cs (0,0,0) B_{iso} / Å^2	0.295(7)	0.704(9)
Mn (½,½,½) B_{iso} / Å^2	0.24(1)	0.52(2)
F (½,½,0) B_{iso} / Å^2	0.32(2)	0.62(3)

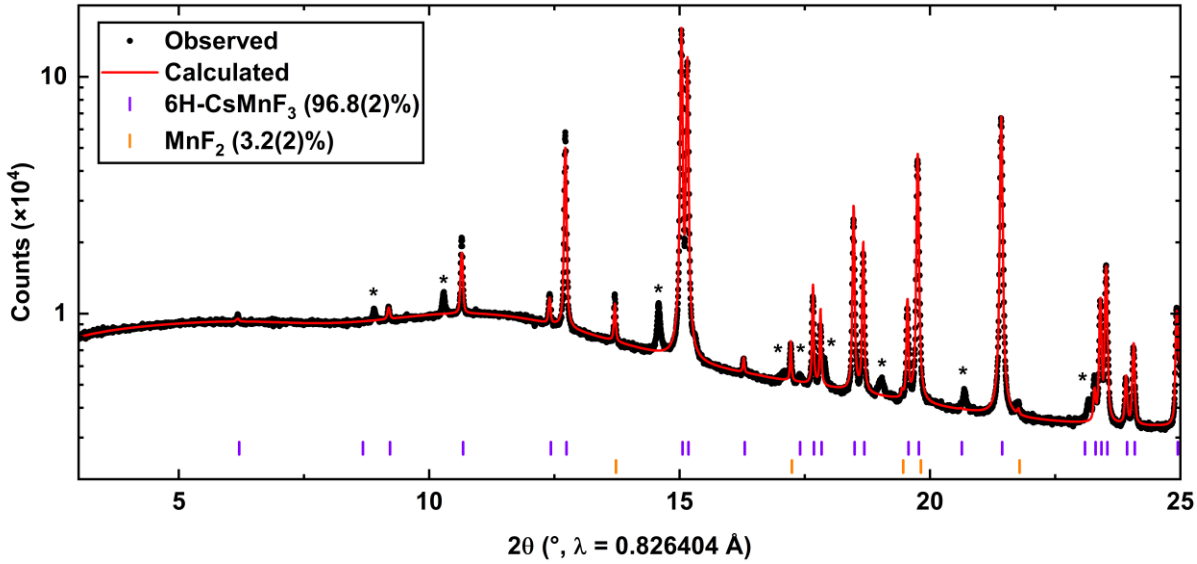

Figure S2. *In situ* synchrotron XRD at 527 °C with a two-phase Rietveld fit with peaks from unidentified new phase(s) highlighted with asterisks. *Y*-axis plotted on a log scale. Phase fractions given in legend do not account for unfitted crystalline phase(s).

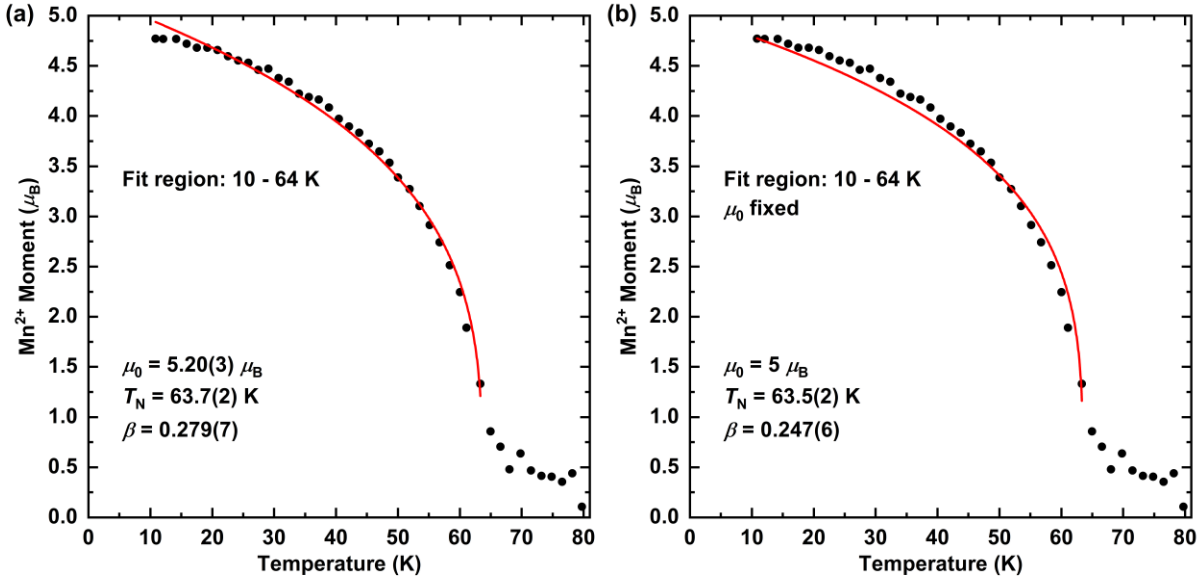

Figure S3. Refined Mn^{2+} moment determined from neutron diffraction as a function of temperature, with critical fits to the full antiferromagnetic region (10 - 64 K) with (a) μ_0 value unconstrained and (b) μ_0 fixed to the theoretical 2*S* moment of 5 μ_B.

References

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[6]Stanley, H. E. *Introduction to phase transitions and critical phenomena*; Oxford University Press, 1987.