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# Optimizing the Preparation of Monoclinic and Pyrochlore $Mn_2Sb_2O_7$

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**Abstract.** Two polymorphs of $Mn_2Sb_2O_7$ have been reported, in the pyrochlore structure and in a chiral, monoclinic structure. In both cases, magnetization data have shown prominent features attributable to a ferrimagnetic impurity. Accessing the intrinsic physical properties of both materials thus requires first making them phase pure. We describe our efforts to optimize the preparation of both polymorphs and how we concluded this was necessary, in hopes that future work will be aided by detailed knowledge of this process.

## 1. Introduction

Strong frustration, in which magnetic interactions compete with each other, impedes spin systems from selecting a unique global ground state at low temperature, leading to a wide variety of physics in which quantum mechanical effects and details of the spins' interactions can be crucial. $Mn_2Sb_2O_7$ can be prepared in the pyrochlore structure (pyr-$Mn_2Sb_2O_7$), shown in Fig. 1(c) and (d), by low-temperature routes[1–4]. This is the most-frustrated known three-dimensional arrangement of magnetic ions, and the quenched orbital moments in pyr-$Mn_2Sb_2O_7$ make it especially interesting. However, preparation by standard solid-state synthesis results in the chiral monoclinic structure m-$Mn_2Sb_2O_7$[5–8] as shown in Fig. 1(a) and (b), which is more closely related to the trigonal Weberites. The Mn sublattice in this structure is built up of $Mn_4$ armchair motifs. Both polymorphs of $Mn_2Sb_2O_7$ are likely to be of considerable interest, but both are readily contaminated by traces of a ferrimagnetic impurity which can obscure the intrinsic physics.

Previous investigation into the magnetic behaviour of the monoclinic polymorph indicated a paramagnetic Curie-Weiss temperature $T_{CW}$ around $-45$ to $-50$ K and a paramagnetic moment corresponding to high-spin $d^5$ $Mn^{2+}$,[9] with a bulk magnetic transition around 13 K. Clear history dependence reported below $\sim$55 K was attributed to an apparent abrupt onset of short-range correlations[9]. Our work (reported elsewhere) concluded, among other results, that the low-temperature transition was intrinsic while the reported history dependence was spurious[8]. Meanwhile, pyr-$Mn_2Sb_2O_7$ had been reported to form a spin glass around 43 K[2, 3], several times *higher* than the bulk magnetic transition reported in the less-frustrated monoclinic polymorph. Our work on the pyrochlore material concluded that this putative spin-glass transition is not

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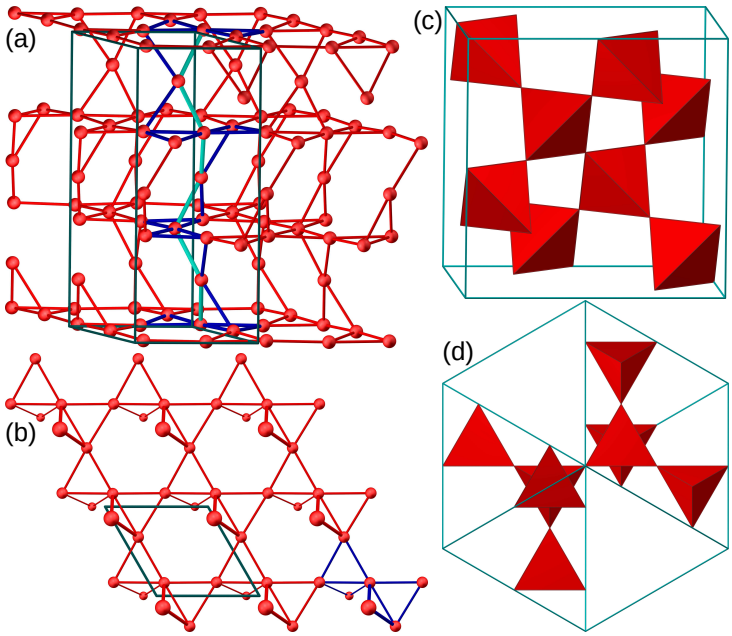


**Figure 1.** Mn sublattices in m-$Mn_2Sb_2O_7$ and pyr-$Mn_2Sb_2O_7$. (a) m-$Mn_2Sb_2O_7$ is composed of $Mn_4$ armchair units — one layer is shown in (b) — adding atoms above and below a kagome plane. The armchairs form helices in the three-dimensional structure, and the shortest bonds in our refinement form a helix along the $c$ axis (ligher-coloured bonds). (c) The pyrochlore structure is composed of corner-sharing $Mn_4$ tetrahedra, with kagome planes perpendicular to all (111) directions (d).

intrinsic, and that the spins actually freeze at a much lower temperature[4]. In both $Mn_2Sb_2O_7$ materials, it would appear that the previous work was limited by phase purity. Since extracting the intrinsic behaviour evidently relies crucially on phase purity, and since we anticipate that other groups will find these materials interesting, this proceedings paper concentrates on how the preparation of these two polymorphs can be optimized.

## 2. Experimental

Powder samples of m-$Mn_2Sb_2O_7$ were prepared in $Al_2O_3$ crucibles in air, from intimately mixed $MnO_2$ (Alfa Aesar, 99.997%) and $Sb_2O_3$ (Alfa Aesar, 99.999%). Mixed powders were calcined typically 2–3 times with intermediate grindings at temperatures between 1050 and 1150°C, typically for 24h per temperature; the mass was monitored for loss of volatile component oxides, and powder diffraction patterns (Rigaku Miniflex II, Cu$K\alpha$ source) were used for initial verification of phase purity. As will be discussed, magnetometry was more sensitive, and in some cases the powder was reground and recalcined as high as 1175°C after magnetic measurements indicated an incomplete reaction.

Powder samples of pyr-$Mn_2Sb_2O_7$ were prepared following the recipe of Brisse[1], with precursor "antimonic acid" first prepared from $SbCl_5$ (Alfa Aesar, 99.997%) and deionized ice water as described in Ref. [10]. The antimony precursor, once dried, was ground with $Mn(Ac)_2{\cdot}4H_2O$ (Aldrich, 99.99%) under ethanol. This starts the reaction, which releases acetic acid and water. The reaction was allowed to continue in an open glass vial at ∼50°C for several days until the material finally dried, at which point it was reground under ethanol. It was then reacted for 12h at each of a series of temperatures from 200 to 550°C in $Al_2O_3$ crucibles in air, typically in steps of 50°C, with intermediate grinding. Powder diffraction and magnetic measurements were again used to verify phase purity and in this case also Mn site occupancy.

Magnetization measurements in fields up to 5 T were performed in a Quantum Design MPMS-XL SQUID magnetometer in RSO mode. Powder samples were packed inside gelatin capsules, which were closed with Kapton tape and loaded into plastic straws. The contribution from the empty sample holder was below the level of the noise. X-ray powder diffraction patterns were collected at key points using a Bruker D8 Discover diffractometer, and the progress of the reaction was monitored using a Rigaku Miniflex II benchtop powder diffractometer, each

with a Cu$K\alpha$ source. Powder neutron diffraction was performed at various temperatures at the ECHIDNA diffractometer at the OPAL research reactor at ANSTO, Australia, from 6.5 to 163.95° in steps of 0.05°, with neutron wavelengths of 1.6620 and 2.4395 Å. Refinements will be reported elsewhere[4, 8].

## 3. Preparation of m-$Mn_2Sb_2O_7$

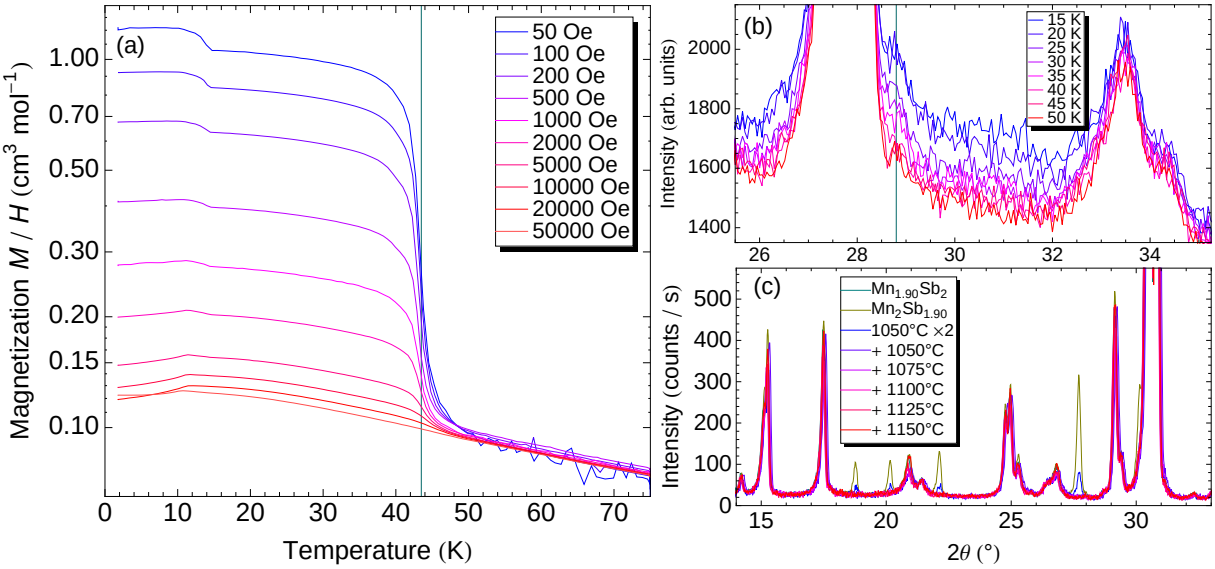


**Figure 2.** a) Temperature-dependent field-cooled magnetization in an early sample that was deemed phase-pure by x-ray diffraction, showing a significant ferromagnetic contribution below ∼43 K. b) A tiny shoulder near 29° in the neutron data, corresponding to the strongest magnetic peak in $Mn_3O_4$, is suppressed around 40 K. c) Impurity peaks were visible for several-percent nonstoichiometry, but extra peaks due to a reduction in symmetry to $P2$ were not affected.

X-ray diffraction found m-$Mn_2Sb_2O_7$ to be phase pure for up to ∼3 % initial cation nonstoichiometry, usually after the second calcine. As shown in Fig. 2a, magnetization measurements at this stage indicated a strong ferro- or ferrimagnetic transition around 43 K. Note that this figure uses a logarithmic vertical scale so that other features remain visible. Neutron diffraction on this material similarly found no obvious impurity peaks, with magnetic Bragg peaks appearing below the ∼13 K transition. There was no evident signature of the dominant magnetic transition around 43 K, which was quite troubling. However, close inspection of the neutron diffraction pattern turned up a tiny hump at the angle corresponding to the strongest magnetic reflection of $Mn_3O_4$ (around 28.8° in Fig. 2b), which disappeared above 40 K. $Mn_3O_4$ is known to have a broad ferrimagnetic transition around 45 K[11, 12]. It was now clear that the most prominent magnetic transition was actually from trace $Mn_3O_4$ impurities that were below x-ray diffraction's detection limit, and that this transition was sufficiently strong, in low fields, to completely swamp the signal from the intrinsic transitions at lower temperature. Magnetization measurements in low field were thus identified as exquisitely sensitive to the presence of this impurity, offering an efficient and effective way to optimize the sample stoichiometry.

In optimizing the preparation conditions for this monoclinic polymorph, several approaches were tried, and it is worth commenting on a few of them. Figure 2c shows diffraction data on samples with ∼5% cation nonstoichiometry, as well as the effect of additional sintering. Peaks associated with Mn impurities were present in samples prepared with a several-percent

excess of Mn (∼5% is shown), and in a sample reacted twice at 1050°C. This latter sample was subjected to a third calcine at 1050°C, then a series of additional firings at progressively higher temperatures. After the third calcine, no traces of impurities were visible in the x-ray pattern, while further steps (below 1250°C) caused no damage to the sample. Magnetization data corresponding to these tests, shown in Fig. 3a, indicate a clear reduction in the $Mn_3O_4$ component with successive firings. So additional calcination steps provided one solution. Given the temperature dependence, this is more likely due to allowing excess volatile oxide components to evaporate, than to allowing an unfinished reaction to reach completion.

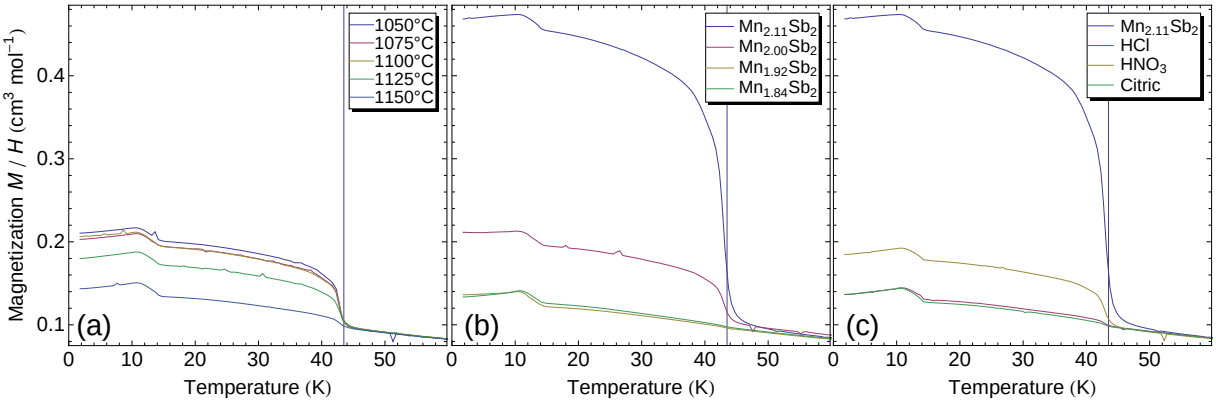


**Figure 3.** Approaches for reducing $Mn_3O_4$ contamination, as characterized by field-cooled magnetization in a field of 50 mT: (a) Additional calcining steps at higher temperatures suppress the $Mn_3O_4$ component. (b) Effect of varying the cation ratio: A small Mn deficiency suppresses the impurity contribution. (c) Effect of various acids, and their Mn-rich starting point.

Tests of the stoichiometry indicated that even a small excess of Sb was sufficient to nearly eliminate the magnetic contribution from $Mn_3O_4$ after the second calcine (Fig. 3b). This presumably either compensates for loss of volatile oxide components or for minor deviations from ideal oxygen stoichiometry in the starting materials. Impurity phases due to excess antimony oxide would not be expected to contribute to the physical properties, since $Sb^{3+}$ and $Sb^{5+}$ are both full-shell, and their oxides are non-magnetic insulators.

Additionally, Mn-rich m-$Mn_2Sb_2O_7$ samples were treated with several dilute (∼10%) acids, to test the acids' ability to dissolve out unreacted Mn oxides. Fig. 3c shows that while HCl, $HNO_3$ and citric acid all worked, best results were obtained using citric acid. The citric acid was prepared from solid granules and was more concentrated.

While additional calcines, a ∼2% Sb excess, and leaching with acid were each able to greatly suppress the magnetic contribution from $Mn_3O_4$, the combination of any two of these approaches was able to fully eliminate this impurity component. We settled on a slight Sb excess coupled with a third sintering, with verification by magnetization measurements. Our final magnetization data for publication were collected on samples subjected additionally to a citric acid treatment, as a precaution.

## 4. Mn-Deficient Pyrochlore

Pyrochlore $Mn_2Sb_2O_7$ is most likely formed by substituting $Mn^{2+}$ for water (or the $2H^+$ on water) in pyrochlore 'antimonic acid' $Sb_2O_5 \cdot nH_2O$ ($n \sim 1.5-2$). If this is performed at sufficiently low temperature, the Sb pyrochlore matrix is retained, and the ultimate product is phase-pure pyr-$Mn_2Sb_2O_7$. As shown in Fig. 4a and highlighted in its inset, as this preparation process progresses there is a gradual decrease in the lattice parameter and an increase in the

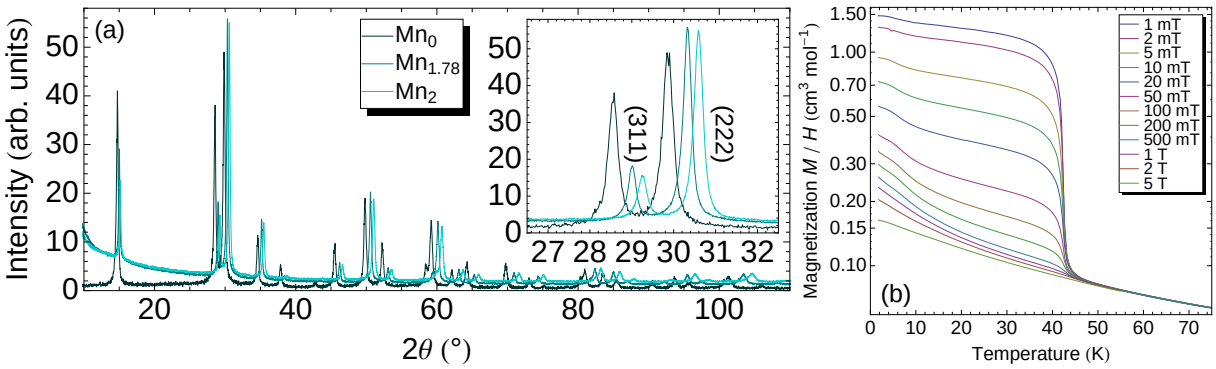


**Figure 4.** (a) X-ray diffraction patterns on samples with different Mn contents. The inset shows the (311) and (222) peaks. (b) Magnetization measurements clearly indicate the presence of unreacted $Mn_3O_4$ in a sample with a small Mn excess.

ratio between the strong (311) and (222) Bragg peaks in x-ray diffraction. The process is continuous, and phase separation is not observed. The peak ratio and lattice parameter thus provide means for optimizing the preparation conditions and monitoring completion of the reaction. This compound is particularly prone to excess Mn due to the variable hydration level $n$ affecting the Sb precursor's molecular weight, and due to the nature of the reaction as a gradual substitution. As in the other polymorph, the clear transition in the magnetization around 43 K arising from ferrimagnetic $Mn_3O_4$ (see Fig. 4b, again using a logarithmic scale) provides an extremely sensitive test for excess or unreacted Mn. In Fig. 4a, the sample identified as $Mn_0$ is the antimonic acid precursor; $Mn_2$ is the fully-reacted, stoichiometric powder, which refined to $Mn_{2.00(5)}Sb_2O_7$ based on x-ray data; and $Mn_{1.78}$ refined to $Mn_{1.78(5)}Sb_2O_7$ if the Mn site was constrained to be either vacant or occupied by Mn.

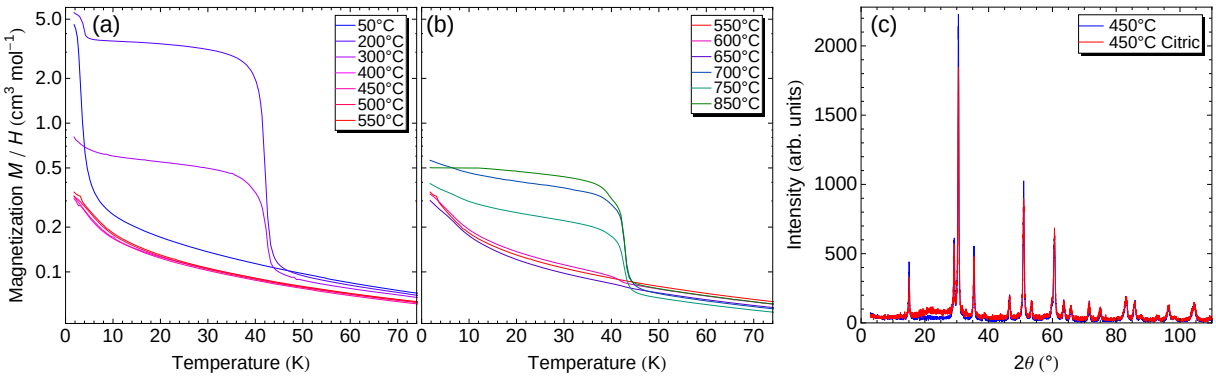


**Figure 5.** (a) Field-cooled magnetization ($H = 10$ mT) after successive heat treatments of the same batch, up to 550°C. (b) Increasing the temperature beyond 550°C eventually leads to decomposition. (c) After calcining at 450°C, a portion of this batch was treated with citric acid, producing a diffuse hump in the diffraction between 15 and 40° and an increase to the (311) peak's relative intensity, suggesting damage to the sample and deintercalation of Mn.

Of the approaches identified for eliminating $Mn_3O_4$ from the monoclinic polymorph, control over the stoichiometry is extremely challenging due to the variable molecular weight of the Sb precursor, but necessary. Heating the sample to higher temperatures causes it to decompose. Acid was found to damage the material somewhat, most likely by leaching Mn atoms back out

of the pyrochlore matrix, reversing the process that put them there. This was manifested as an increase in diffuse x-ray scattering and an increase in the relative intensity of the (311) Bragg peak, as shown in Fig. 5c. However, repeated calcines remain an option, and were ultimately able to produce stoichiometric, $Mn_3O_4$-free samples. Optimal results were obtained for a final calcining temperature of 550°C (see Fig. 5a), with the first hints of decomposition appearing in the magnetization for temperatures of 600–650°C (Fig. 5b) and in the x-ray diffraction pattern by 800°C. By 700°C, there was already an increased diffuse component in the diffraction pattern. The reaction is essentially complete by 400°C, but the magnetization in low fields can continue to show hints of $Mn_3O_4$ for calcines up to 450°C. Ultimately, for the pyrochlore polymorph, we reacted the material for 12 h at each of a sequence of temperatures up to 550°C.

## 5. Conclusion

For both $Mn_2Sb_2O_7$ polymorphs, having phase-pure samples allows us to study the intrinsic magnetic behaviour without interference from other sources of magnetism. The optimized process is described above, and our results on the resulting samples will be reported elsewhere[4, 8]. The bottom line here is that when preparing complex oxide materials for fundamental physics research, it is necessary to be careful, to test for reproducibility, and to be cognizant of what the most likely impurity phases will do if present. We hope that by making a thorough description of our methods and optimization available, this report will aid the community in reproducing our work and more fully investigating these interesting materials.

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