Exploring the Properties of Complex Layered Tin Cluster Compounds

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Solid oxide sintering reactions were used to prepare three new phases with the formula: $Fe_{1+x}Mn_{3-x}Si_2Sn_7O_{16}$ (x = 0.82, 1.65, 2.52). High resolution neutron and synchrotron powder diffraction investigations determined these to be isostructural to the iron rich $Fe_4Si_2Sn_7O_{16}$ phase; space group *P*-3*m*1 (164). Surprisingly, these phases show non-linear changes in unit cell parameters and magnetic behaviour depending on the specific transition metal content, which may indicate that each type of transition metal exhibits a unique set of behaviours that compete rather than cooperate with each other.

1.   Introduction

X-ray powder and neutron powder diffraction experiments have shown that all of the $Fe_{1+x}Mn_{3-x}Si_2Sn_7O_{16}$ (x = 0.82, 1.65, 2.52) phases form trigonal layered materials isostructural to the iron rich phase $Fe_4Si_2Sn_7O_{16}$ described by *Söhnel et. al.*[1]. All members of this solid state series form layered structures that can be viewed as a combination of a pseudo two dimensional layer of oxygen bridged $FeSn_6$ clusters linked by SiO_4 tetrahedra to a second two dimensional layer analogous to a tin substituted fayalite-like layer of MO_6 octahedra with a transition metal to tin ratio of 3:1 through the SnO_6 octahedra (Fig. 1). Ionically it can be broken down as $[(Fe^{2+})_1(Sn^{2+})_6](Fe^{2+})_1(Sn^{4+})_1(Si^{4+})_2(O^{2-})_{16}]$ with the solution of the 18 valence-electron rule for the Fe^{2+} cluster being: $6e^- + 6 \times 2e^- = 18e^-$ (octahedra). The predicted valence state of the Fe and Sn nuclei was confirmed with [57]Fe and [119]Sn Mössbauer spectroscopy [1]. The [57]Fe Mössbauer measurements also showed the presence of both high spin and low spin Fe^{2+} in a ratio of 3:1, indicating the oxide layer sites are all high spin Fe^{2+}. Magnetic measurements confirmed the predicted paramagnetic nature of this material dominating and there was no suggestion of magnetic ordering above 4.2 K.
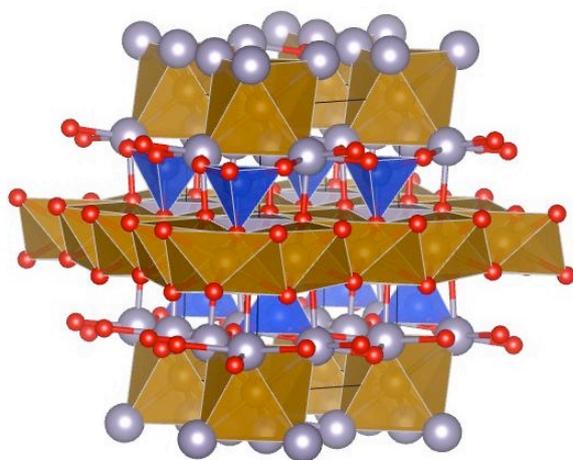
The novel structure of $Fe_4Si_2Sn_7O_{16}$ could however allow for substitution of other high spin nuclei into both of the transition metal crystallographic sites (the MSn_6 cluster and the three transition metal sites in the oxide layer) and presents us a unique opportunity to investigate the engineering of magnetic effects into semiconducting materials by substituting each of the sites by different transition metals. These results will help us to develop a model for synthesis of complex multiferroic stannides to be used in devices with molecular level electronic applications..

Fig. 1. Crystal structure of $Fe_{1+x}Mn_{3-x}Si_2Sn_7O_{16}$.

2. Experimental Details

Highly crystalline powders and single crystals were prepared by solid state sintering by combining the required metal oxide powders together with an excess of tin metal. The samples were places in corundum tubes and sealed under an air atmosphere in quartz tubes. The tubes were heated to 900 ℃ over 48 hours followed by a controlled cooling to 750 ℃ over a period of 200 hours.

Synchrotron X-ray powder diffraction (SXRD) measurements were conducted on the powder diffraction beamline, 10-BM, at the Australian Synchrotron over a 6 to 86° 2θ range with a step size of 0.00375° 2θ, using the MYTHEN detector and the double crystal monochromator of Si(111) flat crystal pair. High resolution neutron powder diffraction measurements (NPD) were carried out using the Echidna instrument located at the OPAL reactor in Sydney, Australia, over a range of 2.75° to 162° 2θ with a step size of 0.125° 2θ at room temperature. Low temperature NPD measurements were carried out using the same parameters with an Oxford Instruments 12T cryomagnet at 5 K at 0 T and 1.8 K between 0 and 10 T using 2 hours per scan. All powder diffraction measurement data sets were refined with the Reitveld method using the FullProf suite software package [2].

^{57}Fe Mössbauer spectra were recorded with transmission geometry in a constant acceleration mode using a ^{57}Co(Rh) source at room temperature in order to determine the valence and spin states of the iron nuclei. Magnetic susceptibility measurements were carried out using a Quantum Design Physical Properties Measurement System (PPMS) under a 1 T magnetic field from room temperature down to 2 K.

3. Results and Discussion

3.1 X-ray Powder Diffraction

High-resolution synchrotron X-ray powder diffraction patterns were collected at the Australian Synchrotron between 6 and 86° 2θ at room temperature to determine the structure of the solid solution $Fe_{1+x}Mn_{3-x}Si_2Sn_7O_{16}$. These measurements confirmed the presence of new phases with a pattern near identical to that of the iron rich phase. However, all mixed Fe/Mn phases showed the presence of a significant amount of SnO_2 contamination indicating an incomplete reaction and/or the oxidation of some of the final products and tin flux during the reaction cooling phase. Rietveld refinements show that as the transition metal ratio trends towards the Mn rich end of the series, there is an increase in the unit cell volume consistent with increasing replacement of Fe^{2+} with Mn^{2+} in line with Vegard's law [3]. However, a more detailed look at the cell parameters show that they increase slightly asymmetrically with the *a/b* parameters increasing more rapidly than that of the *c* parameter. This indicates that the oxide layer transition metal positions rather than the cluster positions were being preferentially substituted. That is be explained by the oxide layer transition metal positions being substituted with Mn as there are three potential transition metal crystallographic positions that lie in that plane rather than two positions which lie in the *c* plane.

Synchrotron measurements from 303 to 823 K were also carried out which allowed us to determine the coefficient of thermal expansion for each of our phases (Fig. 2 and Table 1). These results show a decreasing coefficient of thermal expansion as the phases became richer in Mn, however, the most surprising results showed that the thermal expansion seen is asymmetric in the *a/b* plane with a value of almost double that of the *c* coefficient. Whilst this is commonly seen in most non-cubic materials, the large difference between the *a/b* plane and the *c* plane indicates that this behaviour is related to the layering that we have described in the crystal structure.
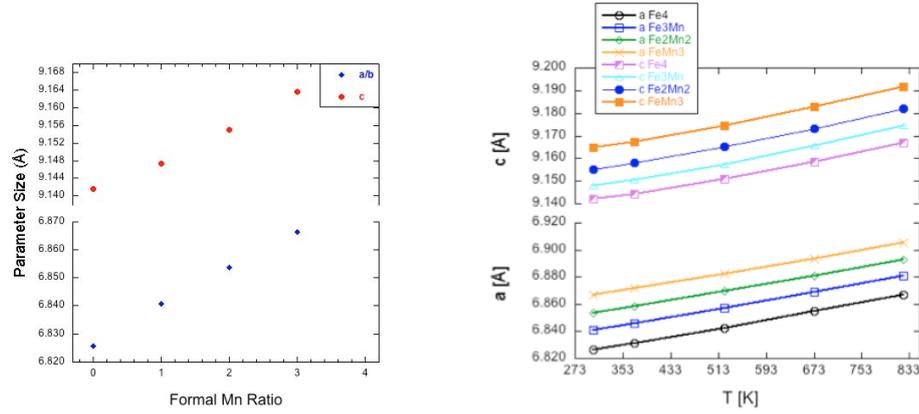
Fig. 2. Cell parameter of $Fe_{1+x}Mn_{3-x}Si_2Sn_7O_{16}$ as a function of composition at room temperature (left) and temperature between 303 K and 823 K (right).

Table 1. Calculated coefficients of thermal expansion.

Formal Phase Composition	αL (a) $[Å.K^{-1}]$	αL (c) $[Å.K^{-1}]$	αV $[Å^3.K^{-1}]$
$Fe_4Si_2Sn_7O_{16}$	1.176×10^{-5}	5.500×10^{-6}	2.912×10^{-5}
$Fe_3MnSi_2Sn_7O_{16}$	1.147×10^{-5}	5.831×10^{-6}	2.888×10^{-5}
$Fe_2Mn_2Si_2Sn_7O_{16}$	1.111×10^{-5}	5.841×10^{-6}	2.820×10^{-5}
$FeMn_3Si_2Sn_7O_{16}$	1.094×10^{-5}	5.837×10^{-6}	2.783×10^{-5}

3.2. Neutron Powder Diffraction

Neutron powder diffraction (NPD) measurements were carried out between 2.75° and 162° 2θ at room temperature in order to refine the occupation of the transition metal positions, the results of these measurements are shown in Table 2. Refinements of all samples were solved for the space group *P-3m1*. Except for the iron rich end member of the solid solution the calculated change in unit cell parameters were within agreement with those obtained from the synchrotron powder diffraction measurements. The elemental occupation refinement of the oxide layer and cluster layer transition metal positions revealed that there was no measurable amount of Mn contained in the Sn_6 clusters. The occupational refinements did however show that the iron rich end member phase was iron and oxygen deficient but this has yet to be explained satisfactorily. For the mixed Fe/Mn phases refinements showed that a significantly lower than expected amount of Mn had been substituted into the oxide layer positions resulting in the phase formulas needing to be recalculated to: $Fe_{1+x}Mn_{3-x}Si_2Sn_7O_{16}$ (x = 0.82, 1.65, 2.52).

Table 2. Unit cell parameter changes for formal and actual fractional change in Mn elemental composition.

Formal Composition	Fe% (refined)	Mn% (refined)	*a/b* [Å]	*c* [Å]	Vol. [Å³]
$Fe_4Si_2Sn_7O_{16}$	100.00	0	6.8322(2)	9.1385(3)	369.42(2)
$Fe_3MnSi_2Sn_7O_{16}$	79.50	20.50	6.8278(2)	9.1331(2)	368.73(2)
$Fe_2Mn_2Si_2Sn_7O_{16}$	58.75	41.25	6.8399(2)	9.1395(2)	370.28(2)
$FeMn_3Si_2Sn_7O_{16}$	37.00	63.00	6.8550(2)	9.1477(3)	372.26(2)

3.3 ^{57}Fe Mössbauer Spectroscopy

^{57}Fe Mössbauer spectra (Fig. 3) were recorded in order to determine the valence state and amount of Fe in each environment for the new phases. The measurements for all phases were resolved using MOSFIT and are resolved into two sets of doublets each phase that show two chemical environments of the iron nuclei present - the cluster and oxide layer positions. No sextets were observed indicating a lack of room temperature magnetic ordering and so these results are typical for paramagnetic Fe^{2+} nuclei [4].
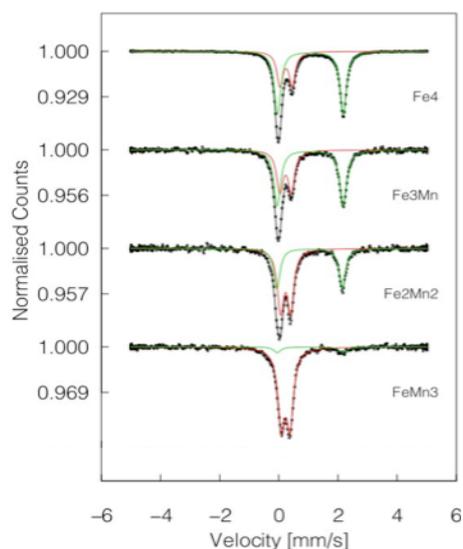

Fig. 3. ^{57}Fe Mössbauer spectra of $Fe_{1+x}Mn_{3-x}Si_2Sn_7O_{16}$

3.4. Magnetic Properties

Magnetic susceptibility measurements were carried out down to 2 K to explore magnetic behaviours of the phases. These measurements show that the Mn richest member $Fe_{1.48}Mn_{2.52}Si_2Sn_7O_{16}$ showed a transition to antiferromagnetic (AFM) ordering at 2.5 K, whilst all other phases remained paramagnetic above 2 °K. These low Curie temperatures are likely due to strong spin-orbit of the Fe^{2+} that prevents the Mn from ordering within the layer. Low temperature (1.8 K) neutron powder diffraction measurements were then carried out under magnetic fields on $Fe_{1.48}Mn_{2.52}Si_2Sn_7O_{16}$ in order to determine the magnetic structures. These powder patterns showed new peaks at low angles – indicating the AFM transition, at low magnetic fields up to about 1 T. These magnetic peaks disappeared at fields above 2 T and the nuclear peaks increased in intensity, which could be a sign of a spin flip transition. However, work is still currently ongoing to explain these results.

References
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