

Structural Properties of Compounds in the $MPS_{3-x}Se_x$ Family

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The families of layered materials MPS_3 and $MPSe_3$ where $M = Mn, Fe, Ni, Zn$ etc shows a wide range of fascinating behaviour, magnetic and structural. The structure of the MPS_3 compounds is monoclinic and the in-plane coordination number is 3. $MPSe_3$ compounds, on the other hand, are rhombohedral. We explore the effect of replacing sulphur with selenium, $MPS_{3-x}Se_x$, and the structural properties of some compounds in this family.

1. Introduction

In this study we investigate both MPS_3 and $MPSe_3$ which are layered quasi two-dimensional materials which have been studied extensively for their interesting structural and magnetic properties [1, 2, 3]. Little if any research has been done on the intermediate compounds of composition $MPS_{3-x}Se_x$ (where $M = Mn, Fe$ and Ni). Because Se is larger than S, if the samples for which $0 < x < 3$ form an isostructural series, the possibility of a systematic study of the behaviour of the two-dimensional magnetism found in these materials arises, particularly as a function of interplanar spacing. This study investigates the structural effect of the substitution of selenium for sulphur ($x = 0, 1, 1.5$ & 2) and determines the point of transition from the monoclinic sulfide structure ($C 2/m$) to the rhombohedral structure of the selenide ($R-3$).

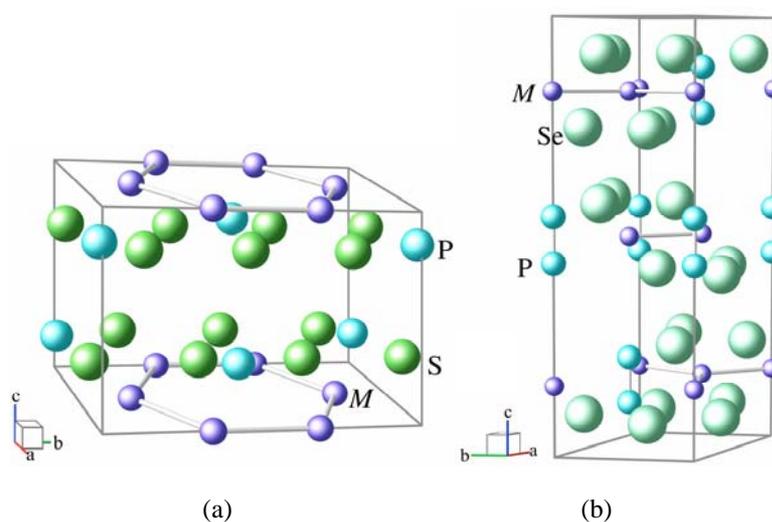


Fig. 1. a) Unit cell of MPS_3 . b) Unit cell of $MPSe_3$. The metal honeycomb lattice is indicated on the sulfide structure. M = metal ion, P = phosphorus, S = sulphur. The structures shown in a) and b) were constructed using data from [4] and [5], respectively, and produced using the *Balls & Sticks* software package [6].

As can be seen in Fig. 1, the unit cell of both MPS_3 and $MPSe_3$ contains a layer of metal ions arranged in a honeycomb lattice (indicated by a hexagon on Fig. 1a). The metal layer lies between layers of S or Se in which the atoms are positioned in a distorted octahedral arrangement around the metal ions [4,5]. Adjacent S, or Se, layers are separated by a Van der Waals gap. Each metal ion hexagon has a phosphorus dimer at the centre.

2. Sample Preparation

The compounds were synthesised from powders of metal sulfide ground with phosphorus, sulphur and selenium powder in stoichiometric ratios and pressed into 6 mm pellets. These were then placed into quartz tubes which were evacuated to 10^{-3} Torr and sealed. The samples were heated to 400°C and held there for a week, then ramped to 700°C and held for a further seven days. This was done to prevent explosions caused by overpressure from the sulphur. Once the compounds were sintered X-ray powder diffraction was used for structural characterisation performed with a Siemens D5000 X-ray diffractometer.

Analysis of the composition and homogeneity of the samples was undertaken using a Hitachi S-4300 scanning electron microscope. The compounds were found to be homogeneous and single phase, with compositional deviations within a few percent. In some cases, most notably the iron compounds, more Se than expected was present, suggesting that S had been lost while heating. The $\text{FePS}_{1.5}\text{Se}_{1.5}$ sample was the most extreme case, with an observed composition of $\text{FePS}_{1.4}\text{Se}_{1.6}$. The NiPS_2Se and FePS_3 sample were within 5% of the desired composition and all other samples were within 2%.

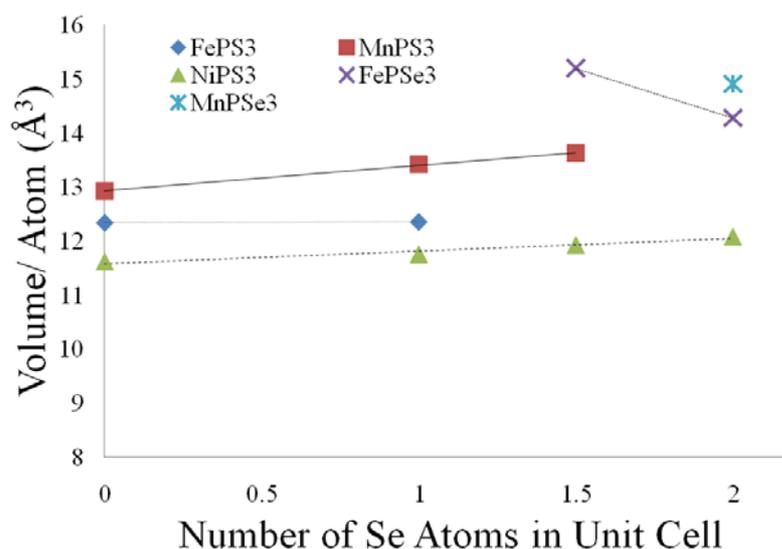


Fig. 2. The change in volume as the number of Se atoms in the unit cell increases for each structure. The error bars are smaller than the data points.

3. X-Ray Diffraction

The diffraction peaks shift towards a smaller 2θ as the concentration of selenium increases and the lattice parameters expand. The change in structure is evident when comparisons are made between diffraction patterns. The number of peaks and relative positions indicate which structure the intermediate compounds form.

The structural characterisation was carried out with reference to the known crystal structures of MPS_3 and MPSe_3 [2,4,5]. Due to massive preferred orientation of the plate-like crystallites, Rietveld refinement of the X-ray data was not possible. The lattice parameters for the samples were determined using Le Bail fitting [7]. As the samples are highly layered the plate-like crystals preferentially align such that the $(00l)$ planes are parallel to the sample surface, which enhances the $(00l)$ reflections and diminishes the $(hk0)$ reflections. This allows reliable determination of lattice parameters, but not of atomic coordinates and displacement parameters.

As expected, on replacing S with Se the lattice parameters expand in order to facilitate the greater size of the Se atom. This can be seen in Fig. 2 and Table 1 for the monoclinic sulfide structure, particularly with reference to $\text{NiPS}_{3-x}\text{Se}_x$, which is monoclinic across the full

composition range. There is insufficient data for the selenide-structure samples to indicate a trend.

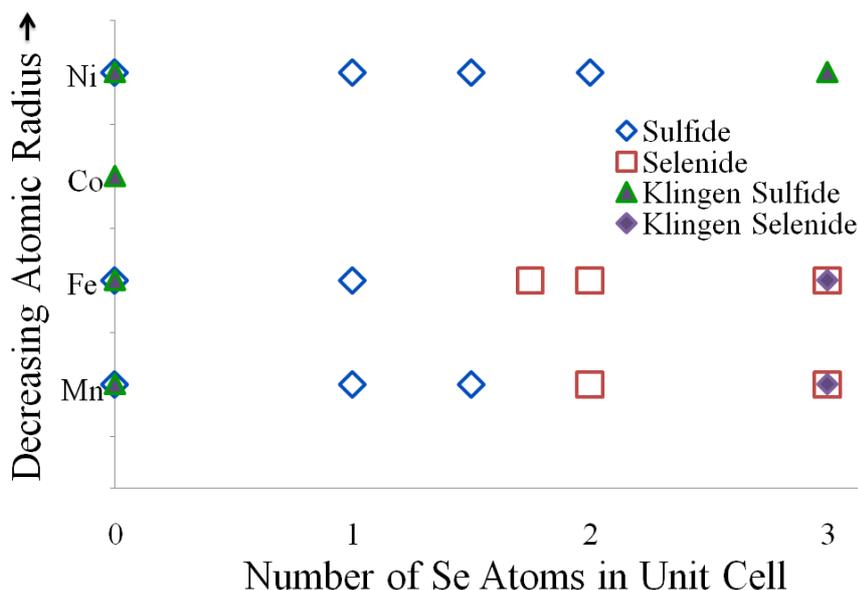


Fig. 3. The change in structure as the number of selenium atoms in the unit cell increases for each set of compounds. Results from this experiment and literature results from Klingen [1] are shown.

4. Discussion

As may be seen in Fig. 3, the nickel compounds do not undergo any structural change as Se level increases, unlike the Mn and Fe samples. The point of transition requires further investigation to determine precisely. Figure 3 shows a phase diagram for this system, and shows that both $\text{FePS}_{3-x}\text{Se}_x$ and $\text{MnPS}_{3-x}\text{Se}_x$ show a transition from the sulphide to selenide structure as a function of composition, with no evidence of a mixed-phase region.

Table 1. Structural parameters for the $\text{MPS}_{3-x}\text{Se}_x$ materials as a function of S:Se ratio. Cell volumes greater than 450 \AA^3 indicate the selenide structure has been formed.

Sample	a (Å)	b (Å)	c (Å)	β (°)	Volume (Å ³)
FePS ₃	5.958(4)	10.31(1)	6.730(4)	107.25(7)	394.93
FePS ₂ Se	5.864(3)	10.335(6)	6.837(1)	107.37(5)	395.45
FePS _{1.5} Se _{1.5}	6.420(5)	6.420(7)	19.593(7)		699.34
FePSSe ₂	6.214(7)	6.214(2)	19.642(8)		656.90
MnPS ₃	6.009(3)	10.59(1)	6.805(3)	107.26(6)	413.66
MnPS ₂ Se	6.086(5)	10.704(8)	6.933(2)	108.04(6)	429.22
MnPS _{1.5} Se _{1.5}	6.1457(3)	10.699(8)	6.988(3)	108.30(8)	436.22
MnPSSe ₂	6.3027(2)	6.3027(3)	19.944(7)		686.11
NiPS ₃	5.808(4)	10.095(5)	6.630(2)	106.94(7)	371.85
NiPS ₂ Se	5.788(3)	10.108(9)	6.739(1)	107.40(8)	376.27
NiPS _{1.5} Se _{1.5}	5.788(4)	10.198(9)	6.770(3)	107.15(6)	381.80
NiPSSe ₂	5.787(4)	10.24(1)	6.841(2)	107.30(7)	386.77

5. Conclusions

The work outlines the first study of the dependence of the structure of $\text{MPS}_{3-x}\text{Se}_x$ materials on the S:Se ratio (Table 1). The point of transition from the monoclinic sulphide structure to the rhombohedral selenide structure lies between FePSSe₂ and FePS_{1.4}Se_{1.6} for

iron-based materials and $\text{MnPS}_{1.5}\text{Se}_{1.5}$ and MnPSSe_2 for Mn-based. There was no evidence of layering of the S and Se, which is to say that, from these experiments, they appear to substitute equally into all sites. From these limited data the transition from monoclinic to rhombohedral structure appears to be direct, rather than via a mixed phase region. Investigation of compositions closer to the critical is expected to prove of interest. The composition at the transition could be determined more precisely by more closely investigating the region of the phase diagram where the transition occurs. Samples of other metals could be investigated to further complete the structure phase diagram. For example, cobalt is of particular interest as it is a member of the first row transition metal series and lies between Ni and Fe in size.

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