



Investigations of the Structural and Magnetic Phase Behaviour of $\text{MnSb}_{2-x}\text{Ta}_x\text{O}_6$ Solid Solutions

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The investigation of the $\text{MnSb}_{2-x}\text{Ta}_x\text{O}_6$ solid solution was designed to study the structural and magnetic transition behavior in this system. A new tetragonal phase (sg. $P4_2/mnm$) was observed for compositions between $x = 1.4$ to 1.6 . This behavior was detected by lab X-ray powder diffraction, THz/IR spectroscopy and soft X-ray absorption spectroscopy. Magnetic susceptibility measurements exhibit an antiferromagnetic ordering over the entire solid solution.

1. Introduction

Recently, the thermodynamically stable modification of MnSb_2O_6 (trigonal, sg. $P321$) has drawn significant attention as it could be an unusual type of multiferroic behaviour and weakly polar material [1]. The structure consists of distorted edge-shared MnO_6 and SbO_6 octahedra with lattice constants of $a = 8.8011(3) \text{ \AA}$, $c = 4.7241(1) \text{ \AA}$ [2]. MnSb_2O_6 shows a magnetic short range ordering below 200 K and long range ordering below 12.5 K, resulting in an incommensurately ordered three-dimensional Heisenberg antiferromagnet [2]. A distorted Mn^{2+} triangular oxide layer induces the frustration of the magnetic ordering below 7.7 K and two possible supercells have been suggested based on neutron powder diffraction experiments (NPD) [2]: an orthorhombic modification ($a, \sqrt{3}a, c$) and a hexagonal modification ($2a, 2a, 2c$). Recent NPD analysis reveals that it can be refined with the trigonal modification with $k = (0, 0, 0.182)$ and it seems not possible to recognize between the magnetic ordering with rotation and amplitude modulation as NPD is not sensitive enough for the cycloidal polarity [1]. MnTa_2O_6 adopts the orthorhombic MgNb_2O_6 structure type (sg. $Pbcn$) [3] with lattice constants $a = 14.4452(2) \text{ \AA}$, $b = 5.76694(9) \text{ \AA}$ and $c = 5.09424(9) \text{ \AA}$ (based on our lab X-ray data refinements). It consists of a layered arrangement of chains of edge-shared MnO_6 and TaO_6 octahedra (Fig. 1). It shows the same orthorhombic magnetic structure as MnNb_2O_6 below the Néel temperature ($T_N = 4.4 \text{ K}$) [3].

The study presented is aimed to investigate the structural and magnetic changes in the solid solution $\text{MnSb}_{2-x}\text{Ta}_x\text{O}_6$.

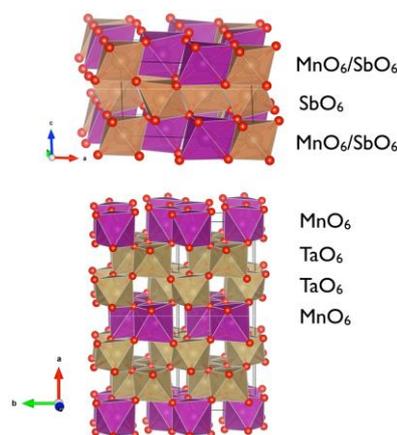


Fig. 1. Crystal structure of MnSb_2O_6 (top) MnTa_2O_6 (bottom).

2. Sample preparation

MnCO_3 , Sb_2O_3 and Ta_2O_5 powder samples were mixed, grinded and placed in corundum boats, heated for 24 hours at $1000 \text{ }^\circ\text{C}$ in a muffle furnace prior to quenching in air yielding in phase pure powders. The samples were re-grinded and re-heated at $1100 \text{ }^\circ\text{C}$ for



further 24-36 hours. Powder samples were initially characterized by X-ray powder diffraction (XRD) using a sealed-tube source (Panalytical Empyrean, monochromated Cu K α radiation, 10 - 80° 2 θ range). IR transmission spectra were collected at the Australian Synchrotron THz/IR beamline joint with Bruker IFS 125/HR Fourier Transform (FT) spectrometer with 6 μ m Multilayer Mylar beam splitter. NEXAFS (Near Edge X-ray Absorption Fine Structure) data were collected from Pohang Accelerator Laboratory (PAL) by elliptically polarized undulator (EPU) beamline at RT. Quantum Design Physical Properties Measurement System (PPMS) was used to collect the magnetic susceptibility data from 2 K to RT in zero field cooled mode (ZFC) with 1 T magnetic field.

3. Results

3.1 X-ray Powder Diffraction Analysis

MnSb_{2-x}Ta_xO₆ (x = 0 to 1) powder diffraction data were collected at RT. Even though the difference in the ionic radii of Ta⁵⁺ (0.64 Å [4]) and Sb⁵⁺ (0.60 Å [4]) is relatively small, the pure Sb and Ta compounds crystallise in significant different crystal structures (Fig. 1). According to X-ray powder diffraction studies (Fig. 2), the formation of a new modification was observed between x = 0.2 to 1.8. The structure can be identified as a tetragonal tri-rutile structure (sg. *P4₂/mnm*), which has been reported for other MSb₂O₆ (M = Co, Ni, Cu) compounds [5]. The powder diffraction data can be refined with a mixture of the trigonal MnSb₂O₆ structure and the new tetragonal modification between x = 0.2 to x = 1.3; the MnSb_{2-x}Ta_xO₆ system turns into a tetragonal sole phase between x = 1.4 to x = 1.6. The lattice parameters are relatively constant between x = 0.2 and x = 1.4, indicating the existence of a large two-phase region between a Sb-rich trigonal structure and a Ta-rich tetragonal structure. Interestingly, the tri-rutile modification has previously been described as a meta-stable modification for MnTa₂O₆ [6]. The orthorhombic modification structure of MnTa₂O₆ can be found between x = 1.7 and x = 2, with an increase of the volume with increasing Ta content (Fig. 3). Overall, three separate solid solutions can be identified: *I* (x = 0 - 0.2): *P321* (MnSb₂O₆ structure type); *II* (x = 1.4 - 1.6): *P4₂/mnm* (MnSb_{2-x}Ta_xO₆ structure); *III* (x = 1.8 - 2.0): *Pbcn* (MnTa₂O₆ structure type).

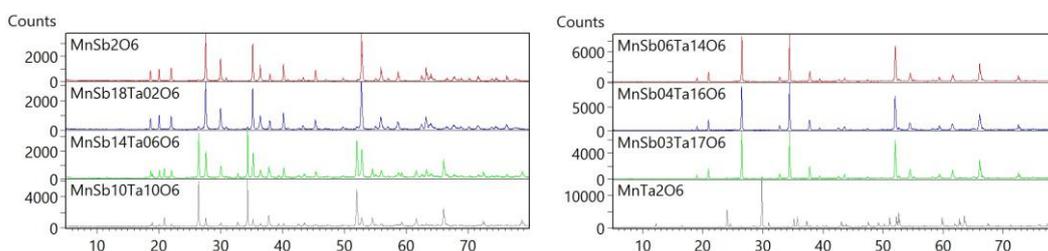


Fig. 2. Lab X-ray powder patterns of MnSb_{2-x}Ta_xO₆.

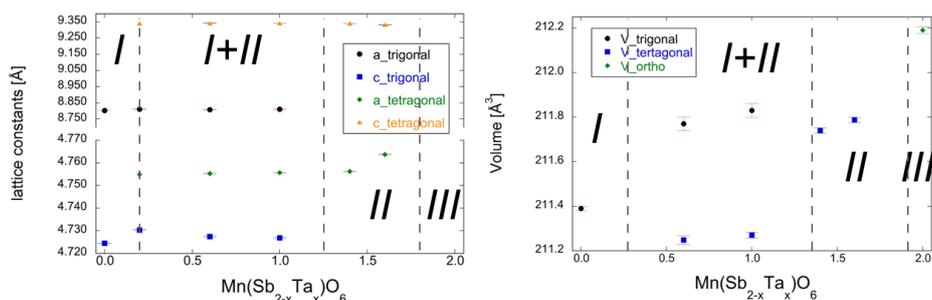


Fig. 3. Lattice constants (left) and adjusted volumes (right) of $\text{MnSb}_{2-x}\text{Ta}_x\text{O}_6$.

3.2 THz/IR Measurements

$\text{MnSb}_{2-x}\text{Ta}_x\text{O}_6$ ($x = 0$ to 1.4) THz/IR transmission data were collected at RT to study the structural behaviour (Fig. 4). Bending or asymmetric stretching of M-O bonds from the structural transition make IR active. For the measurements, the powder samples were mixed with wax. As Fig. 4 shows, it is possible to observe a broadening effect of the spectrum with increasing Ta content. This might be due to the structural phase transition as the distorted crystal structure (trigonal) turns into the non-distorted tetragonal structure for the Ta-rich solid solution *II*. However, the structural transition behaviour can still be detected within the mixture of *I* and *II*. The absorbance peak located at 368 cm^{-1} shows clear intensity decrease behaviour with increasing Ta content. It cannot be observed anymore for $\text{MnSb}_{0.4}\text{Ta}_{1.6}\text{O}_6$ when the crystal structure turns into the tetragonal sole phase. Additional investigations such as low temperature measurements need to be followed to determine whether this peak is a phonon mode or not.

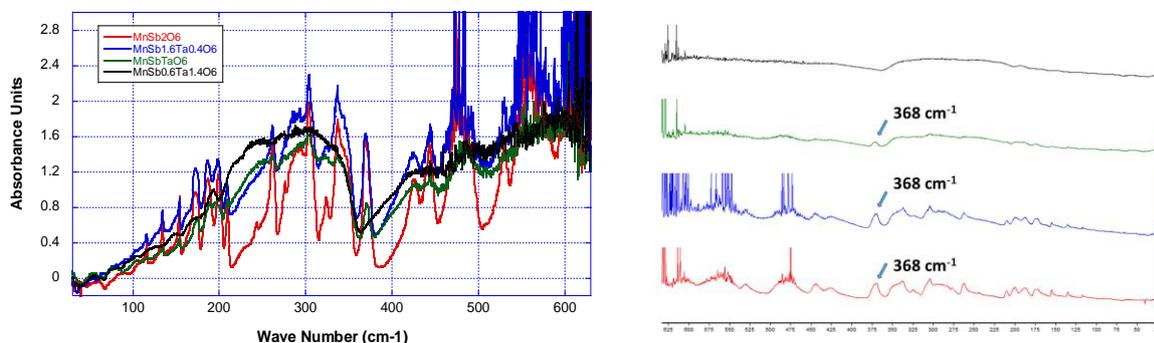


Fig. 4. The calculated absorbance IR spectrum (left) and the stacked view of the normalized absorbance IR spectrum (right) of $\text{MnSb}_{2-x}\text{Ta}_x\text{O}_6$.

3.3 Soft X-ray Measurements

X-ray absorption spectra (XAS) at the $L_{2/3}$ edges were collected at RT to study the electronic structure of $\text{MnSb}_{2-x}\text{Ta}_x\text{O}_6$ (Fig. 5). Mn 2p spectra indicate MnO (Mn^{2+}) type behaviour where the binding energy (Mn $2p_{3/2}$) can be observed around 640.9 eV [7]. It is possible to see a very small 2p XAS peak shifting of the L_3 edge for the samples with different doping Ta ratios. Specifically, $\text{MnSb}_{0.6}\text{Ta}_{1.4}\text{O}_6$ exhibits a relatively clear peak shifting. Peak shifting ($< 1\text{ eV}$) are more likely to emerge due to the differences of the local symmetry around Mn rather than the change of the valence state of Mn [8]. In this case, the shifting can be considered by the different Mn local symmetry as the structural phase transition has been confirmed from the X-ray diffraction from $\text{MnSb}_{0.6}\text{Ta}_{1.4}\text{O}_6$.

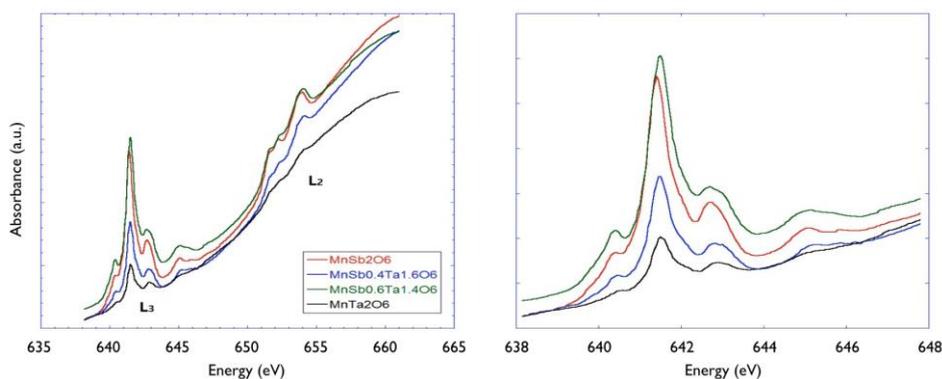


Fig. 5. Mn L₂/L₃ XAS (left) and the expanded view of L₃ edge (right) of MnSb_{2-x}Ta_xO₆.

3.4 Magnetic Measurements

The magnetic susceptibility data of MnSb_{2-x}Ta_xO₆ ($x = 1.4, 1.5, 1.6$) exhibits a similar pattern as MnTa₂O₆, indicating an antiferromagnetic ordering for the tetragonal phase modification of the solid solution *II* (Fig 6). The Néel temperature of MnSb₂O₆ ($T_N = 12.49$ K) is lowered to $T_N = 8.39$ K for MnSb_{0.6}Ta_{1.4}O₆ and it further reduced for MnSb_{0.5}Ta_{1.5}O₆ to $T_N = 7.87$ K. Surprisingly, with even higher Ta content, the Néel temperature increases again, with $T_N = 8.78$ K for MnSb_{0.4}Ta_{1.6}O₆ and $T_N = 9.68$ K for MnTa₂O₆. It also appears that the magnetic susceptibility of the Ta rich compounds of MnSb_{2-x}Ta_xO₆ ($x > 1.5$) have a strong field dependency.

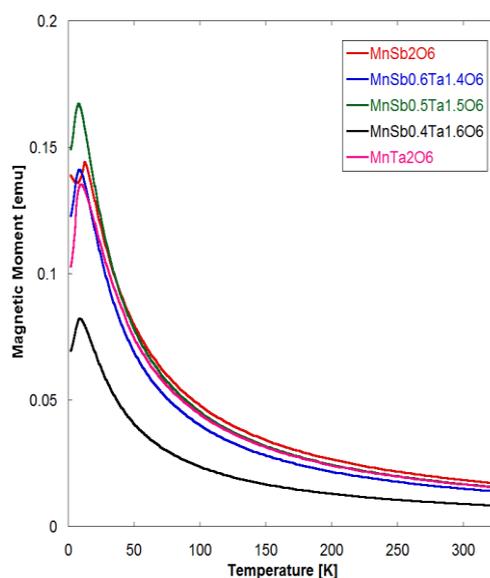


Fig. 6. Magnetic measurements of MnSb_{2-x}Ta_xO₆.

4. Conclusion

The study of MnSb_{2-x}Ta_xO₆ system allows us to investigate the influence of penta-valent Ta doping on the B site of MnSb₂O₆. It could be shown that a new tetragonal phase can be observed from MnSb_{2-x}Ta_xO₆ ($x = 1.4, 1.5, 1.6$) and the antiferromagnetic ordering can be observed from the entire system. More detailed investigation such as neutron powder diffraction will be followed to investigate further with the structural behaviour and the magnetic structure of the Ta doped compounds below the Néel temperature.

Acknowledgments

The authors would like to thank Dr. Dominique Appadoo for the collection of THz/IR data at the Australian Synchrotron and Drs Jae-Young Kim and Yoon-Young Koh for the collection of NEXAFS data at the Pohang Accelerator Laboratory (PAL, Korea). We would like to thank Eva Brücher and Dr. Reinhard Kremer (MPI for Solid State Reserach, Stuttgart, Germany) for the magnetic measurements.



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