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

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The investigation of the MnSb$_{2-x}$Ta$_x$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$_2$O$_6$ (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 $a = 8.8011(3)$ Å, $c = 4.7241(1)$ Å [2]. MnSb$_2$O$_6$ 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$_2$O$_6$ adopts the orthorhombic MgNb$_2$O$_6$ structure type (sg. Pbca) [3] with lattice constants $a = 14.4452(2)$ Å, $b = 5.76694(9)$ Å and $c = 5.09424(9)$ Å (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$_2$O$_6$ below the Néel temperature ($T_N = 4.4$ K) [3].

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

2. Sample preparation

MnCO$_3$, Sb$_2$O$_3$ and Ta$_2$O$_5$ powder samples were mixed, grindend and placed in corundum boats, heated for 24 hours at 1000 °C in a muffle furnace prior to quenching in air yielding in phase pure powders. The samples were re-grounded and re-heated at 1100 °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 Kα radiation, 10 - 80° 2θ 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 μm 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$$_x$Ta$_x$O$_6$ ($x = 0$ to $1$) powder diffraction data were collected at RT. Even though the difference in the ionic radii of Ta$^{5+}$ (0.64 Å [4]) and Sb$^{5+}$ (0.60 Å [4]) is relatively small, the pure Sb and Ta compounds crystallise in significantly different crystal structures (Fig. 1). According to X-ray powder diffraction studies (Fig. 2), the formation of a new modification was observed between $x = 0.2$ to $1.8$. The structure can be identified as a tetragonal tri-rutile structure (sg. $P4_2/mnm$), which has been reported for other MSb$_2$O$_6$ ($M =$ Co, Ni, Cu) compounds [5]. The powder diffraction data can be refined with a mixture of the trigonal MnSb$_2$O$_6$ structure and the new tetragonal modification between $x = 0.2$ to $x = 1.3$; the MnSb$_2$$_x$Ta$_x$O$_6$ 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 MnTa$_2$O$_6$ [6]. The orthorhombic modification structure of MnTa$_2$O$_6$ 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: $I$ ($x = 0 - 0.2$): $P321$ (MnSb$_2$O$_6$ structure type); $II$ ($x = 1.4 - 1.6$): $P4_2/mnm$ (MnSb$_2$$_x$Ta$_x$O$_6$ structure); $III$ ($x = 1.8 - 2.0$): $Pbcn$ (MnTa$_2$O$_6$ structure type).

![Fig. 2. Lab X-ray powder patterns of MnSb$_2$$_x$Ta$_x$O$_6$.](image-url)
3.2 THz/IR Measurements

MnSb$_2$Ta$_x$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 teragonal 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 MnSb$_{0.4}$Ta$_{1.6}$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.

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 MnSb$_2$Ta$_x$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, MnSb$_{0.6}$Ta$_{1.4}$O$_6$ exhibits a relatively clear peak shifting. Peak shifting (< 1 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 MnSb$_{0.6}$Ta$_{1.4}$O$_6$. 

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3.4 Magnetic Measurements

The magnetic susceptibility data of MnSb$_{2-x}$Ta$_x$O$_6$ (x = 1.4, 1.5, 1.6) exhibits a similar pattern as MnTa$_2$O$_6$, indicating an antiferromagnetic ordering for the tetragonal phase modification of the solid solution II (Fig 6). The Néel temperature of MnSb$_2$O$_6$ (T$_N$ = 12.49 K) is lowered to T$_N$ = 8.39 K for MnSb$_{0.6}$Ta$_{1.4}$O$_6$ and it further reduced for MnSb$_{0.5}$Ta$_{1.5}$O$_6$ 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$_{1.6}$O$_6$ and T$_N$ = 9.68 K for MnTa$_2$O$_6$. It also appears that the magnetic susceptibility of the Ta rich compounds of MnSb$_{2-x}$Ta$_x$O$_6$ (x > 1.5) have a strong field dependency.

4. Conclusion

The study of MnSb$_{2-x}$Ta$_x$O$_6$ system allows us to investigate the influence of pentavalent Ta doping on the B site of MnSb$_2$O$_6$. It could be shown that a new tetragonal phase can be observed from MnSb$_{2-x}$Ta$_x$O$_6$ (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.

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References