Influence of Oxygen Defects on the Crystal Structure and Magnetic Properties of the (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$ ($0 \leq x \leq 0.3$) System


Department of Chemistry and Center for Nano Storage Research, National Taiwan University, Taipei 106, Taiwan, Institute of Physics, National Central University, Chung-Li 320, Taiwan, Institute of Materials Manufacturing, Chinese Culture University, Taipei 111, Taiwan, Institute of Optoelectronic Science and Technology, National Taiwan Normal University, Taipei 106, Taiwan, NIST Center for Neutron Research, NIST, Gaithersburg, Maryland 20899-8562, and National Synchrotron Radiation Research Center, Hsinchu 300, Taiwan

Received January 31, 2007

The crystallographic and magnetic behaviors of (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$ ($0 \leq x \leq 0.3$) have been studied by neutron powder diffraction (NPD), synchrotron X-ray powder diffraction, and Raman spectroscopy techniques. Although Na$^+$ ions have larger ionic radii than Tb$^{3+}$ ions, analysis of NPD data reveals a decrease in cell volume upon Na-doping, which can be explained solely by the occurrence of oxygen deficiencies and not by the size effect. The Raman spectrum represents the variation in bond length and bond angle, which originates from the balance of ions, asymmetric structure, and defects in the system. Na-doping causes an oxygen deficiency, and consequently, a peak shift is seen in the Raman spectrum because of the structural adjustment resulting from the doping. The observed effective moments decrease with increasing $x$ because of the replacement of Tb$^{3+}$ ions by Na$^+$ ions. The well-defined peak at $\sim$45 K (labeled $T_{\text{Mn}}$) of the $x = 0.3$ sample is associated with Mn spin ordering, while the magnetic responses associated with $T_{\text{Mn}}$ are not clearly present in the $x = 0.15$ and $x = 0$ samples.

1. Introduction

Multiferroic materials with the coexistence of (anti-)ferromagnetic and (anti)ferroelectric properties have been intensively studied in recent years. The mixed oxides of rare earth and manganese, for example, TbMnO$_3$,1 YMnO$_3$,2 BiMnO$_3$,3 and TbMn$_2$O$_5$,4 display a great variety of magnetic and structural properties have been reported in polycrystalline (Tb$_{1-x}$Ca$_x$)$_2$MnO$_5$5 and single-crystal (Tb$_{1-x}$Gd$_x$)$_2$MnO$_6$6 systems. In the case of doped TbMnO$_3$, the chemical substitution of Tb$^{3+}$ by alkali metal with a formal oxidation state of +1 would be expected to induce more holes in the system and cause an increase in the formal Mn valences. This approach can provide helpful information on the role of the valence of Mn and also about the role of structural change with substitution.7–11

Recently, we synthesized (Tb$_{1-x}$Na$_x$)MnO$_3$ perovskites and studied their crystal structure and electrical properties. We found that the activation energy and resistivity decreased with decreased
increasing Na content.\textsuperscript{12} In addition, we also reported that oxygen content can affect the magnetic structures of both Mn and Tb in TbMnO\textsubscript{3}.\textsuperscript{13} The modulated spin structure of the Mn moments was found to reappear in systems with high Na doping. However, the low-temperature crystallographic behaviors and electron structure properties are still unclear in Na-doped system because of a partial oxygen deficiency.

On the other hand, Raman spectroscopy is a powerful tool for the study of structural disorders, including the dynamic processes. There have been numerous reports on the variations of the Raman spectra of \((R_{1-x}^{3+}A_x^{2+})\text{MnO}_3\) perovskites (\(R = \text{rare earth; } A = \text{Ca, Sr, Ba}; 0 < x < 1\)) with increasing \(x\) values and temperature.\textsuperscript{14–19} As demonstrated, the Raman spectra of doped manganites consist of two or three broad bands at positions close to those of the strongest Raman lines for the parent orthorhombic RMnO\textsubscript{3} compounds with \(Pnma\) structure. Furthermore, the disorder in the doped rare-earth manganites varies strongly with doping level and temperature. Although the role of lattice distortions in the interplay of magnetic and transport properties of \((R_{1-x}^{3+}A_x^{2+})\text{MnO}_3\) is widely recognized, to our knowledge, no experimental reports about Na-doped TbMnO\textsubscript{3} under various temperatures have been published.

In this work, we investigated the crystallographic behaviors of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) (0 \(\leq x \leq 0.3\)) by a combination of neutron powder diffraction (NPD), synchrotron X-ray powder diffraction, and Raman spectroscopy. The electronic structure from X-ray absorption spectra (XAS) measurements at the Mn K-edge and O K-edge is also reported. The influence of oxygen deficiency on the structure and magnetic properties of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) will be discussed.

2. Experimental Section

Polycrystalline samples of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) (0 \(\leq x \leq 0.3\)) were synthesized by conventional solid-state reaction. Detailed sample preparation is described elsewhere.\textsuperscript{12} High-resolution neutron powder diffraction (NPD) patterns were collected on the BT-1 with \(\lambda = 1.5401\ \text{Å}\), a 32-detector powder diffractometer at the NIST Center for Neutron Research, employing a Cu(311) monochromator crystal and 15°-20°-7° FWHM angular collimations. Raman spectra were recorded on a Jobin Yvon T64000 spectrometer in the back-scattering mode, employing a 514.5 nm line from an Ar\textsuperscript{+} laser as the excitation line with an input power of 0.5 mW (at the focus spot, 2–3 µm in diameter). A nitrogen cryostat pump was used to control the sample temperature, and sufficient time was allowed for each temperature change. Smooth upper and bottom surface and thin-pellet powder samples were used to reduce diffuse scattering and temperature differences and to collect all Raman modes simultaneously.

The O K-edge X-ray absorption near-edge structure (XANES) measurements were performed at a 6 m high-energy spherical grating monochromator (HSGM) beamline at the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The absorption spectra were recorded in the X-ray fluorescence-yield (FY) mode using a microchannel plate (MCP) detector consisting of a dual set of MCPs with an electrically isolated grid mounted in front of them. The grid was set to a voltage of 100 V, the front of the MCPs to \(-2000\) V, and the rear to \(-200\) V. The grid bias ensured that positive ions did not enter the detector, while the MCP bias ensured that no electrons were detected. The detector was located parallel to the sample surface at a distance of \(\sim 2\) cm. Photons were incident at an angle of 45° with respect to the sample normal. The incident photon flux was monitored simultaneously.

Figure 1. Observed (crosses), calculated (solid line), and differences (bottom) NPD Rietveld profiles of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) for (a) \(x = 0.15\) and (b) 0.3 at 300 K. Bragg reflections are indicated by tick marks.
by a Ni mesh located after the exit slit of the monochromator. The photon energies were calibrated with an accuracy of 0.1 eV using a Ni mesh located after the exit slit of the monochromator. The X-ray high harmonic was rejected by mirrors. The ion chambers used for measuring the incident (\(I_0\)) and transmitted (\(I\)) beam intensities were filled with a mixture of \(N_2\) and \(H_2\) gases and a mixture of \(N_2\) and \(Ar\) gases, respectively. Energy calibration was carried out by using the first inflection point of the Mn K-edge (6539 eV) absorption spectrum of Mn metal foil as a reference. Reference spectra were simultaneously collected for each in situ spectrum using Mn metal foils.

Synchrotron XRD patterns were taken with a large Debye−Scherrer camera installed at the BL01C2 beam line of NSRRC with \(\lambda = 0.516606\) Å. The sample was contained in a glass capillary tube with an inner diameter of 0.1 mm and was rotated during measurements. The synchrotron XRD data were collected in a 2\(\theta\) range from 0.08 to 28\(\theta\) with a step interval of 0.01°. Structural refinements were made for both the X-ray and neutron diffraction data. Magnetic susceptibilities were carried out between 5 and 300 K by a commercial Quantum Design (PPMS) magnetometer with an ac experimental setup.

3. Results and Discussion

Figure 1a and b shows experimental, calculated, and difference NPD patterns for \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) \((x = 0.15, 0.3)\) at 300 K with \(\lambda = 1.5401\) Å. All the observed peaks can be fitted with the reflection conditions in the orthorhombic \(Pbnm\) space group. The final structural parameters are given in Table 1, and selected bond length and angles

---

**Table 1.** Refined Atomic Positions, Isotropic Thermal Factors, Occupancies, and Reliability Factors of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) in Orthorhombic \(Pbnm\) Space Group from Neutron Diffraction Data at 300 K

<table>
<thead>
<tr>
<th>(x)</th>
<th>(a (\text{Å}))</th>
<th>(b (\text{Å}))</th>
<th>(c (\text{Å}))</th>
<th>(V (\text{Å}^3))</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U_{iso} (\text{Å}^2))</th>
<th>(O(1))</th>
<th>(O(2))</th>
<th>(Mn(4b))</th>
<th>(Tb)</th>
<th>(O(1))</th>
<th>(Mn(4b))</th>
<th>(O(1))</th>
<th>(O(2))</th>
<th>(\rho_H/\rho_{av})</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>5.2996(2)</td>
<td>5.8503(2)</td>
<td>7.4013(2)</td>
<td>229.47(1)</td>
<td>0.099</td>
<td>0.088112(2)</td>
<td>0.55(3)</td>
<td>0.07(4)</td>
<td>0.75(4)</td>
<td>0.85</td>
<td>0.8</td>
<td>0.15</td>
<td>0.2</td>
<td>0.7</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>5.2987(2)</td>
<td>5.8095(2)</td>
<td>7.4106(3)</td>
<td>228.12(2)</td>
<td>0.092</td>
<td>0.07906(2)</td>
<td>0.57(4)</td>
<td>0.07(4)</td>
<td>0.75(4)</td>
<td>0.85</td>
<td>0.8</td>
<td>0.15</td>
<td>0.2</td>
<td>0.7</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td>5.2985(2)</td>
<td>5.7776(3)</td>
<td>7.4152(3)</td>
<td>226.96(2)</td>
<td>0.087</td>
<td>0.07802(3)</td>
<td>0.75(4)</td>
<td>0.07(4)</td>
<td>0.75(4)</td>
<td>0.85</td>
<td>0.8</td>
<td>0.15</td>
<td>0.2</td>
<td>0.7</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>5.2980(3)</td>
<td>5.7496(3)</td>
<td>7.4249(4)</td>
<td>226.17(2)</td>
<td>0.082</td>
<td>0.0772(4)</td>
<td>0.75(4)</td>
<td>0.07(4)</td>
<td>0.75(4)</td>
<td>0.85</td>
<td>0.8</td>
<td>0.15</td>
<td>0.2</td>
<td>0.7</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(\lambda)</td>
<td>0.516606</td>
<td>0.516606</td>
<td>0.516606</td>
<td>(0.516606)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

---

\(\ast\) The strain parameter is defined as \(s = 2(b - a)/a + b\).

**Table 2.** Selected \(\text{Tb}−\text{O}, \text{Mn}−\text{O}\) Distances (Å), and \(\text{Mn}−\text{O}−\text{Mn}\) Angles for the Refinements of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) in Orthorhombic \(Pbnm\) Space Group from Neutron Diffraction Data at 300 K

<table>
<thead>
<tr>
<th>(x)</th>
<th>(\text{Tb}−\text{O}(\text{Mn}(4b)) (\times 2))</th>
<th>(\text{Tb}−\text{O}(\text{Mn}(4b)) (\times 6))</th>
<th>(\text{Mn}−\text{O}(\text{Mn}(4b)) (\times 2))</th>
<th>(\text{Mn}−\text{O}(\text{Mn}(4b)) (\times 6))</th>
<th>(\text{Mn}−\text{O}(\text{Mn}(4b)) (\times 4))</th>
<th>(\Delta\text{Mn}−\text{O}(\text{Mn}(4b)))</th>
<th>(\mu_{fo}(\text{Fe}^{2+}/\text{Fe}^{3+}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>2.3106(2)</td>
<td>2.4733(2)</td>
<td>1.9431(5)</td>
<td>1.9246(6)</td>
<td>2.0672(2)</td>
<td>0.3245</td>
<td>10.7(3)</td>
</tr>
<tr>
<td>0.15</td>
<td>2.3116(2)</td>
<td>2.4734(3)</td>
<td>1.9423(7)</td>
<td>1.9453(8)</td>
<td>2.0484(2)</td>
<td>0.2734</td>
<td>10.4(7)</td>
</tr>
<tr>
<td>0.2</td>
<td>2.3077(3)</td>
<td>2.4739(3)</td>
<td>1.9453(8)</td>
<td>1.9456(7)</td>
<td>2.0440(2)</td>
<td>0.2454</td>
<td>9.7(1)</td>
</tr>
<tr>
<td>0.3</td>
<td>2.2940(4)</td>
<td>2.4742(2)</td>
<td>1.9456(7)</td>
<td>1.9457(7)</td>
<td>2.0429(2)</td>
<td>0.2383</td>
<td>9.1(2)</td>
</tr>
</tbody>
</table>

---

\(\ast\) Some physical parameters obtained from the Curie—Weiss fits are also given.

---

Kitayama’s report. When Na content increases, the total oxygen deficiency and is not caused by the size effect. The volume upon Na-doping can be explained by the occurrence of oxygen occupancy decreases from 3.0 (x = 0) to 2.952 Å (x = 0.3). Furthermore, the decrease in the two basal plane lattice parameters (a and b axes), together with an increase in the axial one (c axis), results in the cell volume becoming smaller (by ~2% from x = 0 to 0.3). It is well-known that the ionic radius of Na\(^{+}\) is larger (1.18 Å) than that of Tb\(^{3+}\) (1.04 Å). Therefore, the decrease in cell volume upon Na-doping can be explained by the occurrence of oxygen deficiencies and is not caused by the size effect.

In Figure 3, the NDP Rietveld of oxygen occupancy is plotted as a function of Na concentration. Some error bars are smaller than the symbol size.

are listed in Table 2. As seen from Table 1, Rietveld analysis afforded sufficiently low R factors. At 300 K, the lattice parameters, as well as the unit cell volume, are plotted as a function of Na concentration in Figure 2. It is worth mentioning that the changes in the lattice parameters and unit cell volume were anisotropic. The decrease in the two basal plane lattice parameters (a and b axes), together with an increase in the axial one (c axis), results in the cell volume becoming smaller (by ~2% from x = 0 to 0.3). It is well-known that the ionic radius of Na\(^{+}\) is larger (1.18 Å) than that of Tb\(^{3+}\) (1.04 Å). Therefore, the decrease in cell volume upon Na-doping can be explained by the occurrence of oxygen deficiencies and is not caused by the size effect.

In Figure 3, the NDP Rietveld of oxygen occupancy is plotted as a function of Na concentration. As noted, the Na-free TbMnO\(_3\) sample is essentially oxygen-stoichiometric, that is, 3-\(\gamma\) ≈ 3.0, which is in good agreement with Kitayama’s report. When Na content increases, the total oxygen occupancy decreases from 3.0 (x = 0) to 2.7 (x = 0.3). Furthermore, the bond valence sum calculated from the refined structure parameters shows that the Mn ions in all of the samples are trivalent. These results indicated that the

Figure 2. Lattice parameters and unit cell volume as a function of Na concentration. Error bars are smaller than the symbol size.

Figure 3. NDP Rietveld of oxygen occupancy as a function of Na concentration. Some error bars are smaller than the symbol size.

Figure 4. Ratio of Mn–O(1)/Mn–O(2)\(_s\) and differences between the Mn–O(2) bond pairs (ΔMn–O(2)) as a function of Na concentration of (Tb\(_{1-x}\)Na\(_x\))MnO\(_3\).
Mn valence of (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$. The Mn K-edge XANES spectra of (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$ are shown in Figure 5a, along with two standards, Mn$_2$O$_3$ (Mn$^{3+}$) and MnO$_2$ (Mn$^{4+}$), for comparison. The weak pre-edge peak labeled A emerges from the 1s → 3d transition caused by pure electric quadrupole coupling or 3d→4p orbital mixing arising from the noncentrosymmetric environment of the slightly distorted octahedral site in the orthorhombic Pbnm space group. The main absorption features labeled B are ascribed to the pure dipole-allowed 1s→4p transition. As the Na content increases, the Mn K-edge XANES spectrum shows systematic changes in the shape and intensity of pre-edge peaks. Especially noteworthy is that peak B does not show a clear shift to higher energy values. The energy position and shape of these absorption features are very similar to those of Mn$_2$O$_3$ standard compounds. This indicates that the valency of Mn ions in (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$ remains nearly 3$^{+}$ with increasing Na content.

So far, we have demonstrated that an increase of Na content in (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$ leads to a reduction in activation energy from 62 (x = 0) to 39 meV (x = 0.3). Here, we examine the detailed electronic structure features. In principle, the positions and intensities of pre-edge peaks in the O K-edge XANES spectra provide significant structural information about the chemical bonding between the ligand and metal atoms. Figure 5b shows the O K-edge XANES spectra of (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$, which exhibit the pre-edge peaks centered at ~530.6 eV, the double peaks at ~535 eV, and a broad structure at ~542 eV. The pre-edge peaks below 531.1 eV of the O K-edge absorption spectra correspond to the transition of the oxygen 1s electron to the hybridized state of Mn 3d and oxygen 2p orbitals, whereas the broad peaks above 542 eV correspond to the transitions to hybridized states of oxygen 2p and Mn 4sp orbitals. As noted, the pre-edge peak position remains nearly constant throughout all Na concentrations. The variation of the integrated intensity of the pre-edge peak of (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$ gives important information on the hole distribution on Mn–O sites because the density of an unoccupied state is related to the hybridization of Mn 3d-O 2p orbitals. The shaded area in Figure 5b is the integrated pre-edge intensity corresponding to an oxygen 2p orbital hybridized with a Mn 3d band. The variations of normalized integrated intensity of the pre-edge region of the O K-edge XANES spectra of (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$

Figure 5. (a) Mn K-edge XANES spectra of (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$ along with two standards of Mn$_2$O$_3$ (Mn$^{3+}$) and MnO$_2$ (Mn$^{4+}$) for comparison. (b) O K-edge XANES spectra of (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$. Variations of pre-edge peak intensity of the O K-edge absorption spectra of (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$ are given in the inset.

Figure 6. Temperature dependence of the magnetic susceptibility ($\chi'$) of (Tb$_{1-x}$Na$_x$)MnO$_{3-y}$ (x = 0, 0.15, and 0.3). Inverse susceptibility (1/$\chi'$) is also shown in the inset. The oscillating magnetic field has an amplitude of 1 Oe and a frequency of 100 Hz.

are shown in the inset of Figure 5b. The pre-edge peak intensity discontinuously increases with increasing Na content from \( x = 0 \) to 0.3, and the spectral weight of the pre-edge peak slightly increases, by 3%, from \( x = 0 \) to 0.3 in \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\). The results indicate that the hole concentration in \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) shows a slight increase when the Na content is increased.

Figure 6 depicts the in-phase component (\( \chi' \)) of the ac magnetic susceptibility of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\), \( x = 0, 0.1, 0.2, \) and 0.3. The high-temperature portions of all the \( \chi'(T) \) curves were fitted to Curie–Weiss behavior (solid curves in the inset), and the results are listed in Table 2. The Curie constants were converted into effective moments by \( \mu_{\text{eff}} = 2.83 \times (MC)^{1/2} \), where \( M \) is molecular weight and \( C \) is Curie constant in units of emu K g\(^{-1}\) Oe. Obviously, the effective moments decrease with increasing \( x \) simply because of the replacement of Tb\(^{3+} \) ions by Na\(^{+} \) ions. The well-defined peak at \( \sim 45 \) K, labeled \( T_{\text{Mn}} \), in the \( \chi'(T) \) plot of the \( x = 0.3 \) sample is associated with Mn spin ordering,\(^1 \) while the magnetic responses associated with \( T_{\text{Mn}} \) are not clearly present in the \( x = 0.15 \) and 0 samples. We believe that the oxygen deficiency in the MnO\(_6\) octahedron may weaken the interaction strength between Mn ions and give a high magnetic response signal in an ac susceptibility experiment. This implies that, in this system, oxygen ions are mediated between Mn ions and play an important role in both ferromagnetic (FM) nearest-neighbor (NN) and antiferromagnetic (AFM) next nearest-neighbor (NNN) superexchange (SE) spin interactions.\(^{13,33} \) The oxygen vacancies not only caused the interaction path to break but also shorten the distance between Mn ions, which implies that the NN interaction is much preferred at higher Na-doping levels. The transition from NNN to NN interactions with increasing Na-doping will create interactions along the two crystallographic directions at an appropriate Na-doping concentration (\( x = 0.15 \)) and become almost similar. That would cause the magnetic structure changes from incommensurate (\( x = 0 \)) to simple commensurate (\( x = 0.15 \)) and then back to incommensurate (\( x = 0.3 \)), and it would also change the \( T_c \) value from \(-12\) K (\( x = 0 \)) to \(-4\) K (\( x = 0.15 \)) and to \(-21\) K (\( x = 0.3 \)), as shown in Table 2. Briefly, the competition between the NNN and NN interactions creates an intermediate state at around \( x = 0.15 \), which brings simple commensurate magnetic structure and higher \( T_c \). Moreover, it also reveals that the anomaly at around 9 K, labeled \( T_{\text{Tb}} \), appears only in the undoped sample. Therefore, the substitution of more Na ions on the Tb site will weaken the rare-earth interaction and dilute the average rare-earth moment in each unit cell.

Raman scattering is an excellent tool for the study of crystal symmetry and its change with doping. The vibration modes allowed in the R MnO\(_3\) compounds have been identified with increasing Na content from \( x = 0 \) to 0.3, and the spectral weight of the pre-edge peak slightly increases, by 3%, from \( x = 0 \) to 0.3 in \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\). The results indicate that the hole concentration in \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) shows a slight increase when the Na content is increased.

![Figure 7](image1)

**Figure 7.** (a) Raman spectrum of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\), \( x = 0, 0.1, 0.2, \) and 0.3) at 300 K. (b) Raman shift as a function of Na concentration.

**Table 3.** Raman Shifts Identified of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\), \( x = 0, 0.1, 0.2, \) and 0.3)

<table>
<thead>
<tr>
<th>no.</th>
<th>( T ) (cm(^{-1}))</th>
<th>AS (cm(^{-1}))</th>
<th>B (cm(^{-1}))</th>
<th>SS (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>371.5(5)</td>
<td>479.4(4)</td>
<td>521.9(5)</td>
<td>607.4(5)</td>
</tr>
<tr>
<td>0.1</td>
<td>364.0(6)</td>
<td>471.6(4)</td>
<td>520.5(7)</td>
<td>606.1(7)</td>
</tr>
<tr>
<td>0.2</td>
<td>372.5(7)</td>
<td>477.6(9)</td>
<td>524.2(9)</td>
<td>609.0(4)</td>
</tr>
<tr>
<td>0.3</td>
<td>367.8(7)</td>
<td>473.1(8)</td>
<td>524.2(6)</td>
<td>607.1(4)</td>
</tr>
</tbody>
</table>

![Figure 8](image2)

**Figure 8.** (a) Raman spectra of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\), \( x = 0.2 \) at 300 K. (b) Thermal evolution of Raman spectra with fitted peak position (black line).

Influence of Oxygen Defects on \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\)

identified. For \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_{3-y}\), the \(\text{Pbnm}\) symmetry allows 24 active Raman modes of \((7\text{A}_g + 7\text{B}_{1g} + 5\text{B}_{2g} + 5\text{B}_{3g})\). Martín-Carrón\(^{35}\) et al. labeled five observed Raman modes of \(\text{RMnO}_3\) as \(R\) for rare-earth ion mode at \(250\ \text{cm}^{-1}\), \(T\) the tilt, \(\text{A}_g\) mode at between \(280\) and \(370\ \text{cm}^{-1}\), \(\text{A}_g\) for asymmetric stretch \(\text{A}_g\) mode at around \(480\ \text{cm}^{-1}\), \(B\) the bending \(\text{A}_g + \text{B}_{1g}\) mode between \(420\) and \(530\ \text{cm}^{-1}\), and \(SS\) for the symmetric stretch, \(\text{B}_{1g}\), around \(610\ \text{cm}^{-1}\). Recently, Iliev\(^{37}\) et al. reported a series of Raman experiments of the single-crystal \(\text{RMnO}_3\). They pointed out that some normal modes of the Martín-Carrón notation should be corrected. We used Martín-Carrón’s notation with Iliev’s corrections in this paper. Figure 7a shows the Raman spectrum of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_{3-y}\) \((x = 0, 0.1, 0.2, \text{and } 0.3)\) samples. Each solid curve sketched on the data points represents the fitted result with a combination of five Lorentz profiles (not shown). The fitting parameters are plotted and listed in Figure 7b and Table 3, respectively. A small perturbation of the peak positions was found as \(x\) is increased for \(T\), \(\text{AS}\), \(B\), and \(SS\) modes, which originate from structural distortion. The Na-doping causes oxygen deficiency and, consequently, the inner structure adjustment, and in turn, it exhibits a peak shift in the Raman spectrum. For the \(x = 0.2\) sample, we performed the Raman and X-ray diffraction experiments in temperature-controlled circumstances to study the relation between structure parameters and the Raman mode in detail. Figure 8a depicts the Raman shifts of the \(x = 0.2\) sample at \(300\ \text{K}\), and Figure 8b shows thermal evolution of the Raman spectra with fitted peak positions (black line). It was found that the sample showed four features labeled as \(T\), \(\text{AS}\), \(B\), and \(SS\) at around \(370\), \(479\), \(520\), and \(610\ \text{cm}^{-1}\), respectively.\(^{35}\)

Figure 9. Temperature dependence of Raman frequency of (a) tilt modes, (b) bending modes, and (c) stretching modes for \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_{3-y}\) \((x = 0.2)\). The X-ray diffraction experiments by refined lattice parameters and some selected bond lengths and angles are give on the right axis for comparison.

and one second-order Raman scattering attributed mainly to
the oxygen vibration mode at 650 cm\(^{-1}\).\(^{37}\) In particular, the
trace of all peaks does not shift monotonically as the
temperature is increased. It is known that the T, AS, B, and
SS modes depend on the Mn−O(1)−Mn angle, Mn−O
length, Mn−O length, and Tb−O(1) length, respectively. For
comparison, the temperature dependence of the Raman
frequencies of the (a) tilt mode, (b) bending modes, and (c)
stretching modes for the 0.2 sample are given in Figure
9. These parameters were obtained from Lorentz fitting of
Raman spectrum and X-ray refinement by the GSAS
program. From the feature near 370 cm\(^{-1}\) (as seen in Figure
9a), which is assigned as T/A\(_g\)(4) normal mode (Figure 9d),
it is clear that the peak is highly dependent on the tilt angle
between the two octahedra as the temperature changes. It is
interesting that the opposite evolution curve is present
between the tilt angle and Raman shift as the temperature
was varied, which is different from Martín-Carrón’s\(^{35}\) report.
They replaced the R ion with a bigger one which makes a
smaller tilt angle and also press the octahedra (chemical
pressure), which implies that the system needs more energy
to drive this mode. In our case, tilt angle changes are only
casted by the various temperatures so that it is easier to drive
(thermal energy 1 K, \(\sim 0.083\) meV, Raman shift 1 cm\(^{-1}\),
\(\sim 0.124\) meV), while the tilt angle is larger and the peak
appears at a smaller Raman shift position. In Figure 9b and
e, the bending mode which is assigned as B/A\(_g\)(3) + mixed
\(\sim 520\) cm\(^{-1}\) includes two different A\(_g\)(3) normal modes.
This indicates that, inside the MnO\(_6\) octahedron, the angle
between the O(1)−Mn−O(1) axis (almost along the c axis)
and the Mn−O(2) plane is bent (as shown in Figure 9d),
and the mixed modes are a combination of the A\(_g\)(3)
and A\(_g\)(1) modes. It is easy to understand that a shorter
Tb−O(1) bond length will bend the octahedron and bring
about a larger force constant, indicating that higher frequency
excitation is needed. Moreover, Figure 9c reveals the relation
between Mn−O length and both AS/A\(_g\)(1) (\(\sim 480\) cm\(^{-1}\)) and
SS/B\(_{2g}\)(1) peaks (\(\sim 610\) cm\(^{-1}\)). The stretching mode includes
symmetric and antisymmetric stretching, which vibrates
along Mn−O bonds in- or out-of-phase. The in-phase term
of most kinds of vibration motions depend on shorter bond
lengths/force constants, and the out-of-phase term is the
opposite. This is also in agreement with the sketch in Figure
9c. The observation of these non-monotonically contracting
bond lengths and angles with decreasing temperature origin-
ated from the balance of ion bonding, asymmetric structure,
and defects in the system.

4. Conclusions
The crystallographic and magnetic properties of perov-
skite-related \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_{3-y}\) compounds in the composi-
tional range of \(0 \leq x \leq 0.3\) are reported. We demonstrate
that the oxygen deficiency in \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_{3-y}\) plays an
important role in controlling the crystal structure and
magnetic properties. An increase in the Na content leads to
a reduction in the octahedral distortion and JT effect.
Moreover, we found that the oxygen vacancies not only
casted the interaction path to break but also caused the
distance between Mn ions to shorten, which implies that the
NN interaction is preferred at higher Na-doping levels.

Acknowledgment. We thank the National Science Coun-
cil of Taiwan under Grant 95-2113-M-002-009 and the
Ministry of Economic Affairs of Taiwan under Grant 95-
EC-17-A-08-S1-0006 for financial support.

IC070190F