Crystal Structure, Magnetic and Electrical Properties of (Tb$_{1-x}$Na$_x$)MnO$_3$

$x = 0$ and 0.15

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We have investigated the crystal structure, magnetic and electrical properties of (Tb$_{1-x}$Na$_x$)MnO$_3$ ($x = 0$ and 0.15). These materials have been prepared in polycrystalline by solid-state reaction. The orthorhombic structure with space group $Pbnm$ is observed in these materials. (Tb$_{1-x}$Na$_x$)MnO$_3$ samples exhibit paramagnetic to antiferromagnetic transition temperature of $\sim 10$ K and $\sim 20$ K for $x = 0$ and $x = 0.15$ samples respectively. The corresponding transition temperature is increased with increasing Na content. Moreover, a decrease in $E + W$ value from 62 meV ($x = 0$) to 38 meV ($x = 0.15$) was found. This may be due to the reduction of activation energy and resistivity in the parent compound by Na substitution.

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I. INTRODUCTION

In recent years, the rare-earth manganites have been the subject of considerable investigation since the discovery of their colossal magnetoresistance (CMR) properties [1, 2]. Hole-doped manganites ($\text{R}_{1-x}\text{M}_{x}$)MnO$_3$ ($\text{R}$=rare earth; $\text{M}$=divalent alkaline earth cation) display a great variety of magnetic structure [3, 4] and charge ordering phenomena [5, 6]. In fact, the perovskite structure is observed for $\text{RMnO}_3$ oxides with large-sized $\text{R}^{3+}$ cations ($\text{r}_{\text{c}}^{3+}$) under ordinary synthesis conditions, crystallize in a hexagonal non-perovskite structure of space group $P6_3$cm [8]. Moreover, the hexagonal compounds can be modified to perovskites under high temperature and high pressure environment [9, 10]. In the recent report, Kimura et al. [11] have grown single crystals of $\text{TbMnO}_3$ and they found gigantic magnetoelectric and magnetocapacitance effects, which can be attributed to the switching of electric polarization induced by magnetic fields. Moreover, the spontaneous electric polarization $P$ parallel to the $c$ axis appears below $T_{\text{lock}}$, which is defined as incommensurate-commensurate (or lock-in) transition temperature [11]. To our knowledge there is no report available on the evolution of the magnetic and magnetotransport properties for (Tb$_{1-x}$Na$_x$)MnO$_3$ system which may
be similar to the system of (Tb$_{1-x}$Ca$_x$)MnO$_3$ reported by Blasco et al. [12]. In this article we aim to investigate in detail the crystal structure, magnetic and electrical properties of (Tb$_{1-x}$Na$_x$)MnO$_3$ ($x = 0$ and 0.15) samples due to chemical substitution of the bigger Na$^+$ ions in place of smaller Tb$^{3+}$ ions, which may induce an internal chemical pressure. Most interestingly, we demonstrate the dramatic changes of magnetic and transport properties upon tuning the Na doping amount in Tb sites.

II. EXPERIMENTAL

The samples of (Tb$_{1-x}$Na$_x$)MnO$_3$ ($x = 0$ and 0.15) were prepared by solid state reaction. Stoichiometric mixtures of high purity powders of Tb$_4$O$_7$, NaCO$_3$ and MnCO$_3$ were sintered in air at 1450°C for 24 h. X-ray diffraction (XRD) measurements were carried out on a SCINTAG (X1) diffractometer (Cu K$_\alpha$ radiation, $\lambda = 1.5406$ Å) at 40 kV and
30 mA. The GSAS program [13] was used for the Rietveld refinements in order to obtain information on the crystal structures of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) \((x = 0\) and \(0.15\)). The scanning electron micrograph (SEM) pictures were recorded at room temperature by Philips XL30 SEM equipped with a field emission gun at 15 kV. The resistivity measurements were performed with a four-probe technique. Magnetization measurements were performed on a SQUID magnetometer (Quantum Design PPMS) from 0 to 350 K.

III. RESULTS AND DISCUSSION

Fig. 1(a) and (b) display the observed and calculated XRD patterns at 300 K of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) \((x = 0\) and \(0.15\)) samples. All the observed peaks can be indexed on the basis of an orthorhombic unit cell (space group: \(Pbnm\)). The morphology and particle size of the \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) \((x = 0\) and \(0.15\)) samples were investigated by means of SEM and are shown in Fig. 2. An increase in the particle size with increasing Na content \((\sim 6\) and \(12\mu\text{m}\) for \(x = 0\) and \(x = 0.15\), respectively) is observed which indicates the incorporation of Na into Tb sites improves grain growth during the sintering process. Fig. 3 shows the temperature dependence of magnetization at a magnetic field of 0.1 T for \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) \((x = 0\) and \(0.15\)) samples. The results show paramagnetic to antiferromagnetic transition temperature of \(\text{Tb}^{3+}\) moment at \(\sim 10\) K for \(x = 0\). The corresponding transition temperature is increased with increasing Na content. This result shows a similar behavior of Ca doped sample reported by Blasco et al. [12]. Fig. 4(a) shows the temperature dependence of resistivity of \((\text{Tb}_{1-x}\text{Na}_x)\text{MnO}_3\) \((x = 0\) and \(0.15\)) compounds in the absence of a magnetic field. Both \(x = 0\) and \(0.15\) samples show an insulator behavior over the whole temperature range.
down to around 225 K and 155 K, respectively. Based on the small polarons model from the Jahn-Teller distortion of strong lattice-electron interaction, the $E + W$ values ($E$: the energy required to produce intrinsic carriers; $W$: the polaron formation energy) can be calculated [14]. Fig. 4(b) shows the $\log\rho/T$ vs. $1/T$ curves of (Tb$_{1-x}$Na$_x$)MnO$_3$ ($x = 0$ and 0.15) samples. The activation energy obtained from the electrical transport is proportional to the band gap. A decrease in $E W$ values from 62 meV ($x = 0$) to 38 meV ($x = 0.15$) indicates that the Na doping causes reduction in activation energy and resistivity.

IV. CONCLUSIONS

In summary, we have investigated the crystal structure, magnetic and electrical properties of (Tb$_{1-x}$Na$_x$)MnO$_3$ ($x = 0$ and 0.15). Moreover, we demonstrate the dramatic changes of magnetic and transport properties upon tuning the Na doping amount in the Tb site. The Na-doped sample has a higher paramagnetic to antiferromagnetic transition temperature of the Tb$^{3+}$ moment and lower conductivity as compared to that of undoped one.

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FIG. 4: (a) Temperature dependence of resistivity ($\rho$) of (Tb$_{1-x}$Na$_x$)MnO$_3$ ($x = 0$ and 0.15). (b) The log $\rho/T$ vs. $1/T$ curves of (Tb$_{1-x}$Na$_x$)MnO$_3$ ($x = 0$ and 0.15).

References

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