Effects of Mn substitution on the thermoelectric properties of the electron-doped perovskite Sr$_{1-x}$La$_x$TiO$_3$

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Abstract. We have tried to improve the n-type thermoelectric properties of the electron-doped Perovskite Sr$_{1-x}$La$_x$TiO$_3$ by a Mn substitution. The 1 ~ 2 % Mn substitution enhances the Seebeck coefficient ($S$) and reduces the thermal conductivity ($\kappa$) by about 50 % at room temperature (RT) without largely increasing the resistivity for the 5 % electron-doped SrTiO$_3$. Consequently, the power factor at RT keeps a large value comparable to that of Bi$_2$Te$_3$ and the dimensionless figure-of-merits at RT increases twofold by the slight Mn substitution. Such a large reduction of $\kappa$ at RT is perhaps due to the effect of Jahn-Teller active Mn$^{3+}$ ions, around which dynamical local lattice distortion may occur.

1. Introduction
Since the good p-type thermoelectric (TE) property was found in Co oxides [1], transition metal oxides have been expected to be next generation TE materials, because of abundant natural resources and being nontoxic, environmental benign, and stable at high $T$. However, there is a problem to be solved in oxide TE materials. Good n-type oxide TE material being a counterpart of Co oxide has not been found till now, while several oxides, such as ZnO [2], SrTiO$_3$ [3, 4], CaMnO$_3$ [5], Fe pnictides [6, 7, 8], and etc., were known to show relatively good n-type TE properties.

Electron-doped perovskite SrTiO$_3$ is one of good candidates of n-type oxide TE materials. The power factor ($PF = \frac{S^2}{\rho}$) at room temperature (RT) is comparable to that of Bi$_2$Te$_3$ [3], but the dimensionless figure-of-merit ($ZT = \frac{S^2T}{\rho\kappa}$) is about 0.1 at RT [3] and about 0.3 at 1000 K [4]. There have been many attempts to improve the TE properties by various methods [9, 10].

In this study, we have tried to improve the TE properties of the electron-doped perovskite Sr$_{1-x}$La$_x$TiO$_3$ by a Mn substitution. We have found the Mn substitution enhances $ZT$ up to about 0.15 at RT. The enhancement of $ZT$ is due to the enhancement of the Seebeck coefficient ($S$) and the large reduction of the thermal conductivity ($\kappa$) without a large increase of resistivity ($\rho$). In this proceeding, the origins of the changes of these physical properties will be discussed.
2. Experimental procedures

Crystals of $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-y}\text{Mn}_y\text{O}_3$ were grown by a floating zone method. The starting materials were $\text{SrCO}_3$, $\text{La}_2\text{O}_3$, $\text{TiO}_2$, and $\text{MnCO}_3$. $\text{La}_2\text{O}_3$ was dried in air at 1000 °C for 12 hours before use. The stoichiometric mixture ($\text{Sr} : \text{La} : \text{Ti} : \text{Mn} = 1-x : 1 : 0$ or $1-x : x : 0.98 : 0.02$) of starting materials were ground, calcined at 1000 °C for 12 hours, reground, calcined at 1300 °C for 12 hours, pressed into a rod, and sintered in air at 1350 °C for 12 hours. The crystal growth was performed at a rate of 30 - 35 mm/hour with rotation of the feed and seed rods in opposite directions in a flow of pure Ar gas.

Crystal structures and compositions for the obtained samples were investigated by the powder X-ray diffraction measurements and inductive coupled plasma (ICP) mass spectroscopy measurements, respectively. $\rho$ of the obtained crystals was measured by the conventional four-probe method below 300 K by using a cryogen free cryostat. $S$ and $\kappa$ were simultaneously measured in a vacuum ($\sim 10^{-6}$ torr) by the steady method by using a handmade measurement system in a cryostat.

3. Results and discussions

3.1. Lattice parameters and compositions of $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-y}\text{Mn}_y\text{O}_3$

Powder X-ray diffraction measurements of the obtained samples indicate no impurity phase and they also indicate that the obtained crystals have a cubic structure with a space group of $\text{Pn3m}$ (No. 221). Figure 1 shows the nominal Mn concentration ($y$) dependences of lattice parameters of the obtained $\text{SrTi}_{1-y}\text{Mn}_y\text{O}_3$ and $\text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_{1-y}\text{Mn}_y\text{O}_3$ crystals deduced from the Rietveld analysis of the powder XRD patterns. If the Mn ions are not lost during the crystal growth, $y = z$. The lattice parameter for $\text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_{1-y}\text{Mn}_y\text{O}_3$ monotonically increases with the increase in $y$, while that for $\text{SrTi}_{1-y}\text{Mn}_y\text{O}_3$ monotonically decreases with the increase in $y$. These results indicate at least that the Mn$^{3+}$ ions are produced at the Ti site in $\text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_{1-y}\text{Mn}_y\text{O}_3$, since the size relation of ion radii ($d$) in six-fold coordination ($B$ (Ti) site) is $d(\text{Mn}^{3+}) < d(\text{Ti}^{4+}) < d(\text{Mn}^{2+})$ and that in twelve-fold coordination ($A$ (Sr) site) is $d(\text{Mn}^{2+}) < d(\text{Sr}^{2+})$.

![Figure 1](image1.png)  
**Figure 1.** Nominal Mn concentration ($y$) dependences of lattice parameters ($a$) for $\text{SrTi}_{1-y}\text{Mn}_y\text{O}_3$ and $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{1-y}\text{Mn}_y\text{O}_3$.

![Figure 2](image2.png)  
**Figure 2.** La substitution ($x$) dependence of the quantity of Mn cation ($z$) for $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{0.98}\text{Mn}_z\text{O}_3$ ($y = 0.02$).

However, according to ICP mass spectroscopy measurements, the quantity of Mn cation ($z$) for the obtained Mn substituted electron-doped SrTiO$_3$ crystal is smaller than the nominal one ($y$). Figure 2 shows the La substitution ($x$) dependence of the quantity of Mn cation ($z$) for $\text{Sr}_{1-x}\text{La}_x\text{Ti}_{0.98}\text{Mn}_x\text{O}_3$, whose nominal value of $z$ ($= y$) is 0.02. As shown in Fig.
2, the observed quantities of Mn cation are smaller than the nominal ones and the quantity monotonically increases with the increase in $x$. Then, the obtained Mn substituted crystal for $x = 0.05$ which shows the better TE properties (as will be discussed later) actually becomes $\text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_{0.98}\text{Mn}_{0.0126}\text{O}_3$ with lattice defects. This reduction of Mn ions is consistent with the observed absolute value of magnetization ($M$) smaller than the expected values of $M$ which well obeyed the Curie-Weiss law. The spin quantum number of Mn ions estimated from the corrected $M$-$T$ curve is much larger than 1.5, which also indicates that Mn$^{3+}$ or Mn$^{2+}$ ions are produced in $\text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_{0.98}\text{Mn}_{0.0126}\text{O}_3$.

3.2. Effects of Mn substitution on the thermoelectric properties of the electron-doped SrTiO$_3$

Figure 3 shows $T$ dependences of $\rho$, $S$, and $\kappa$ for $\text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_3\text{O}_3$ and $\text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_{0.98}\text{Mn}_{0.0126}\text{O}_3$ crystals, the latter of which shows the best TE property in this study.

![Figure 3](image1.png)

**Figure 3.** (Color online) Temperature dependences of (a) resistivities ($\rho$), (b) Seebeck coefficients ($S$), and (c) thermal conductivities ($\kappa$) for $\text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_{1-y}\text{Mn}_y\text{O}_3$.

![Figure 4](image2.png)

**Figure 4.** (Color online) Temperature dependences of (a) power factors ($PF$) and (b) dimensionless figure-of-merits ($ZT$) for $\text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_{1-y}\text{Mn}_y\text{O}_3$. 


As shown in the Fig. 3(a), \( \rho \) slightly increases by the Mn substitution and the increase of \( \rho \) is almost constant below RT, which is perhaps due to the introduction of Mn ions and lattice defects. The absolute value of \( S (|S|) \) also increases by the Mn substitution. (Fig. 3(b)) According to the Hall measurements, the estimated carrier concentration \( n \) for \( \text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_{0.98}\text{Mn}_{0.012}\text{O}_3 \) \( (\sim 7 \times 10^{20} \text{cm}^{-3}) \) is about 10 % smaller than that of \( \text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_3 \) \( (\sim 8 \times 10^{20} \text{cm}^{-3}) \), which should cause the increase of \( |S| \). However, if the effective mass and relaxation time of electron is assumed to be invariant, the observed increase of \( |S| \) \( (\Delta S \sim 30 \mu \text{V/K at RT}) \) cannot quantitatively be explained only by the decrease of \( n \). Additional reason is necessary to fully explain the change. It is interesting that \( \kappa \) at RT decreases by about 50 % with the Mn substitution. (Fig. 3(c)) In comparison with those by the other substitutions \([4, 11]\), the reduction by the slight Mn substitution is rather dramatic.

Figure 4 shows \( T \) dependences of \( PF \) and \( ZT \), deduced by using the measured \( \rho \), \( S \), and \( \kappa \). Although \( \rho \) increases with the Mn substitution, since the \( |S| \) increases, the deduced \( PF \) at RT keeps the relatively large value comparable to that of \( \text{Bi}_2\text{Te}_3 \). Furthermore, since \( \kappa \) decrease by about 50 % at RT, the \( ZT \) value increases twofold at RT. The observed \( ZT \) value is about 0.15 at RT, which is the best value among the reported ones for bulk electron-doped \( \text{SrTiO}_3 \).

3.3. Origin of the reduction of thermal conductivity by the Mn substitution

The possible origins for the dramatic reduction of \( \kappa \) of the La and Mn cosubstituted compounds are the effects of the produced Mn\(^{3+} \) ions at the Ti sites and the lattice defects due to a loss of Mn ions. Since \( \kappa \) of \( \text{SrTi}_{0.98}\text{Mn}_{0.022}\text{O}_3 \) having more lattice defects (Fig. 2) is as large as that of non-doped \( \text{SrTiO}_3 \) at RT (not shown), the reduction of \( \kappa \) of \( \text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_{0.98}\text{Mn}_{0.012}\text{O}_3 \) is not thought to be due to the effect of lattice defects. Furthermore, taking into account the size relation of ion radii in six-fold coordination \( (B (\text{Ti}) \) site), since the lattice parameters decreases with the increase of Mn in \( \text{SrTi}_{1-y}\text{Mn}_y\text{O}_3 \) \([12]\) (Fig. 1), the Mn ions in \( \text{SrTi}_{0.98}\text{Mn}_{0.022}\text{O}_3 \) are thought to be Mn\(^{4+} \) at the Ti sites. Then, these results indirectly indicate that the strong candidate of the origin of the reduction of \( \kappa \) for the La and Mn cosubstituted \( \text{SrTiO}_3 \) is the effect of the produced Mn\(^{3+} \) ions at the Ti sites. The Mn\(^{3+} \) ion in six-fold coordination is a so called Jahn-Teller active ion, around which local lattice distortion occurs. Such a local lattice distortion around the Jahn-Teller active ions perhaps causes the reduction of \( \kappa \). Furthermore, since, in comparison with the results of other substitutions \([4, 11]\), the reduction is rather dramatic, the local lattice distortion may not be static but dynamic one which should effectively reduce \( \kappa \). Lastly, it should be mentioned that the observed reduction of \( n \) in \( \text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_3 \) by the Mn substitution may originate from localization of a part of doped-electrons at the Mn ions placed at the Ti sites. Such localization of electrons at the Mn ions should change the Mn\(^{4+} \) ions at the Ti sites to the Jahn-Teller active Mn\(^{3+} \) ions.

4. Summary

We have tried to improve the thermoelectric (TE) properties of the electron-doped perovskite \( \text{SrTiO}_3 \) by a Mn substitution at the Ti sites and found that the dimensionless figure-of-merit for \( \text{Sr}_{0.95}\text{La}_{0.05}\text{Ti}_{0.98}\text{Mn}_{0.012}\text{O}_3 \) was about 0.15 at RT. The relatively good n-type TE property for the compound was due to the enhancement of Seebeck coefficient \( (S) \) and the large reduction of thermal conductivity \( (\kappa) \) without a large increase of resistivity by the slight Mn substitution. The enhancement of \( S \) is partially due to the reduction of the carrier (electron) concentration perhaps due to localization of a part of doped-electrons at the Mn ions, although additional reason is necessary to fully explain the enhancement. Such localization of electrons at the Mn ions should lower the valence of Mn ions at the Ti sites to trivalent, i.e. it should produce a Jahn-Teller active Mn\(^{3+} \) ions. The Mn\(^{3+} \) ions at the Ti site may produce dynamical local lattice distortion around the ions, which may cause the dramatic reduction of \( \kappa \). Further macroscopic
and microscopic experimental investigations, such as specific heat measurements and neutron scattering measurements, are desired to evaluate the scenario.

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