

# Size Effect of A-site Cation on n-type Thermoelectric Properties in CaMnO<sub>3</sub>-based System

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## Abstract

The thermoelectric (TE) properties of the electron-doped (RE<sub>x</sub>AE<sub>1-x</sub>)MnO<sub>3</sub> (RE: rare earth ions such as La, Pr *etc.*, AE: the alkaline earth ions such as Ca, Sr *etc.*, X=0.05, 0.10) have been investigated as a function of the average ionic radius  $r_A$  of the A-site cation in the perovskite structure (AMnO<sub>3</sub>). The electrical resistivity  $\rho$ , Seebeck coefficient  $S$  and the thermal conductivity  $\kappa$  change depending on  $r_A$ . Near the room temperature, the figure of merit  $Z$  shows a maximum at  $r_{A(\text{opt})}=1.182\sim 1.184\text{\AA}$ , which is realized for the La<sub>0.10</sub>Ca<sub>0.90</sub>MnO<sub>3</sub> and La<sub>0.05</sub>(Ca<sub>0.98</sub>Sr<sub>0.02</sub>)<sub>0.95</sub>MnO<sub>3</sub>. The 5% substitution by elements M with varying valencies for the Mn-site degrades the TE properties in the La<sub>x</sub>Ca<sub>1-x</sub>(Mn<sub>0.95</sub>M<sub>0.05</sub>)O<sub>3</sub> (X=0.05, 0.10) due to the disorder in the MnO<sub>6</sub> network. The cracks, inevitably induced in the samples especially for the small X region, seriously reduce the TE properties.

## 1. Introduction

Since the discovery of the high thermoelectric (TE) performance in NaCo<sub>2</sub>O<sub>4</sub> [1], the TE properties of the oxides have been widely investigated. The TE module using only the p- and n-type oxides has been fabricated and operated [2]. Compared with higher p-type TE performance in NaCo<sub>2</sub>O<sub>4</sub>, the TE potential of the n-type oxides is, at present, lower for the practical use. The electron-doped M<sub>x</sub>Ca<sub>1-x</sub>MnO<sub>3</sub> shows a relatively high TE performance among oxides and is a possible candidate of the n-type TE materials. The substitution for the Ca-site by Bi has presented the best figure of merit  $Z$  for X=0.05~0.10 [3]. Ohtaki *et al.* investigated the 10% substitution effect for the Ca-site by several elements M in the (M<sub>0.10</sub>Ca<sub>0.90</sub>)MnO<sub>3</sub> system [4]. It was found that the electrical conductivity  $\sigma$  at 300 K increased with increasing average ionic radius of the (M<sub>0.10</sub>Ca<sub>0.90</sub>)-site resulting in M=Bi being the best element for the thermoelectricity. The origin of the high performance comes from the increase of the carrier mobility  $\mu$  caused by the larger intersite distance for hopping. However, there have been no systematic investigations as for the size effect of the A-site cation of the perovskite structure (AMnO<sub>3</sub>) on the TE properties including the Ca-site substitution by divalent ions.

In this study, we investigate the relation between the average ionic radius  $r_A$  of A-site cation and the thermoelectricity (the figure of merit  $Z$  and the power factor  $P$ ) in (RE<sub>x</sub>AE<sub>1-x</sub>)MnO<sub>3</sub> (RE=rare earth ions, AE=alkaline earth ions) at the concentration of X=0.05 and 0.10. The  $r_A$  value determines the lattice distortion from the cubic through the tolerance factor  $\Gamma=(r_A+r_O)/\sqrt{2}(r_{Mn}+r_O)$ ,  $r_{Mn}$  and  $r_O$  being the ionic radii of Mn and oxygen) and the one-electron bandwidth is broadened as  $\Gamma$  approaches 1. The variance  $\sigma^2$  of

the A-site ionic radius ( $=\sum y_i r_i^2 - r_A^2$ ,  $y_i$  being the fractional occupancy of the A-site species and  $r_i$  being its ionic radius) also affects the magnetic transition [5]. We also report the substitution effect of the Mn-site by several elements M with various ionic valencies on the thermoelectricity in La<sub>x</sub>Ca<sub>1-x</sub>(Mn<sub>0.95</sub>M<sub>0.05</sub>)O<sub>3</sub> (X=0.05 and 0.10). The relation between the thermoelectricity and the lattice distortion and the variance  $\sigma^2$  is discussed for the electron-doped system.

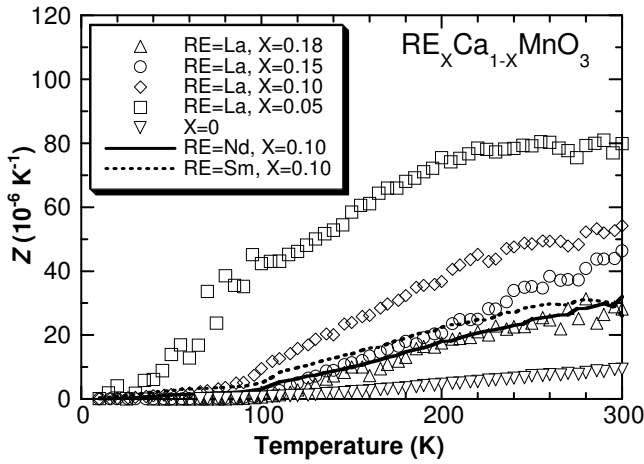
## 2. Experimental

The several series with  $1.17\text{\AA}\leq r_A\leq 1.20\text{\AA}$  of RE<sub>0.10</sub>Ca<sub>0.90</sub>MnO<sub>3</sub> (RE=Dy, Gd, Sm, Nd, Pr, La), La<sub>0.10</sub>(Ca<sub>1-y</sub>Sr<sub>y</sub>)<sub>0.90</sub>MnO<sub>3</sub> (0.05 $\leq y\leq 0.4$ ) and La<sub>0.05</sub>(Ca<sub>1-y</sub>AE<sub>y</sub>)<sub>0.95</sub>MnO<sub>3</sub> (AE=Sr, Ba: 0.02 $\leq y\leq 0.05$ ) were fabricated by a solid state reaction method. The La<sub>x</sub>Ca<sub>1-x</sub>(Mn<sub>0.95</sub>M<sub>0.05</sub>)O<sub>3</sub> (M=Mg<sup>2+</sup>, Al<sup>3+</sup>, Sn<sup>4+</sup>; X=0.05 and 0.10) samples were also fabricated. The  $r_A$  value, the tolerance factor  $\Gamma$  and the radius variance  $\sigma^2$  were calculated from the tabulated radii with 9-fold coordination [6]. The mixtures of raw powders were calcined at 1000 °C for 24 h in air, pressed into pellets and then sintered at 1400 °C for 8 h in air. Some of the samples were heat-treated in flowing oxygen at 900 °C for 24 h in order to achieve the oxygen stoichiometry. The measured densities of samples were about 85~90 % of the ideal ones. The X-ray diffraction analyses at room temperature confirmed that all the samples were in a single orthorhombic phase. The electrical resistivity  $\rho(T)$  was measured by a standard four-terminal method from 10 K to 300 K. The thermal conductivity  $\kappa(T)$  and Seebeck coefficient  $S(T)$  were measured by a steady-state heat flow method. The carrier mobility  $\mu$  and the carrier concentration  $n$  were estimated measuring the Hall coefficient at room temperature.

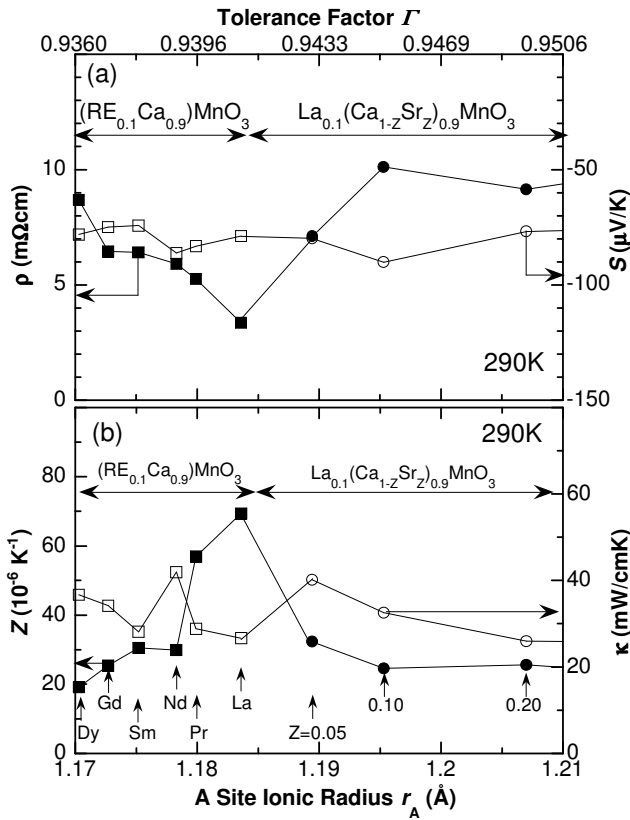
## 3. Results and Discussion

### 3.1 (RE<sub>x</sub>AE<sub>1-x</sub>)MnO<sub>3</sub> system (X=0.05, 0.10)

Fig. 1 shows the temperature dependence of the figure of merit  $Z(T)$  of the La<sub>x</sub>Ca<sub>1-x</sub>MnO<sub>3</sub> and RE<sub>0.10</sub>Ca<sub>0.90</sub>MnO<sub>3</sub> (RE=Nd, Sm). The  $Z$  values of all the samples decrease with decreasing temperature  $T$ . In La<sub>x</sub>Ca<sub>1-x</sub>MnO<sub>3</sub>, the  $Z$  value near the room temperature takes a maximum at X=0.05 and then decreases with increasing X. The electrical resistivity  $\rho$  and the Seebeck coefficient  $S$  decrease with increasing X at room temperature, while the thermal conductivity  $\kappa$  remains nearly constant. Then the  $Z$  enhancement at X=0.05 comes from the relatively large  $S$  and small  $\rho$  values near the optimum electron doping level. It has been found that the number of cracks in the samples increases for 0 $\leq X\leq 0.05$  and that the existence of the cracks reduces the  $Z$  value causing the



**Figure 1:** The temperature dependence of  $Z(T)$  of the  $\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$  and  $\text{RE}_{0.10}\text{Ca}_{0.90}\text{MnO}_3$  (RE=Nd, Sm).



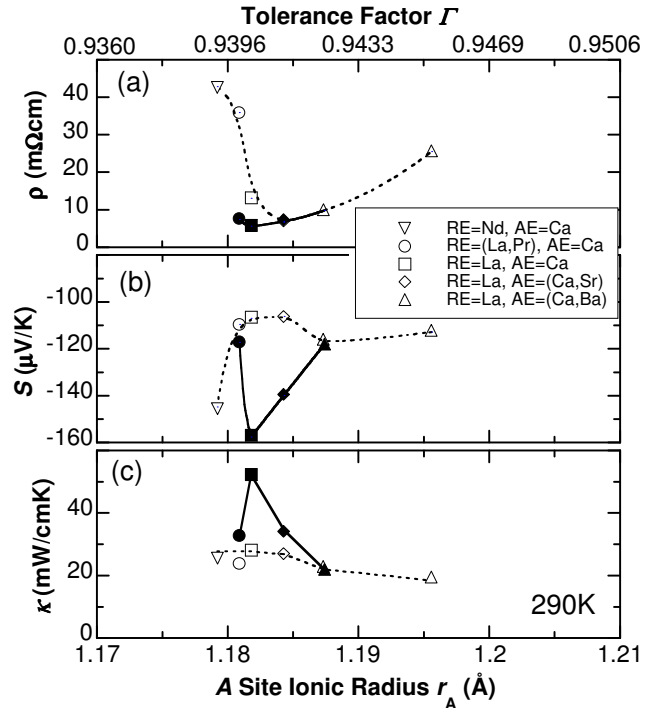
**Figure 2:** (a)  $\rho$  and  $S$ , (b)  $\kappa$  and  $Z$  for  $\text{RE}_{0.10}\text{AE}_{0.90}\text{MnO}_3$  at 290 K as a function of  $r_A$ .

increase in  $\rho$ . The  $Z$  value for  $\text{RE}_{0.10}\text{Ca}_{0.90}\text{MnO}_3$  (RE=Nd, Sm) is lower than that for the RE=La sample.

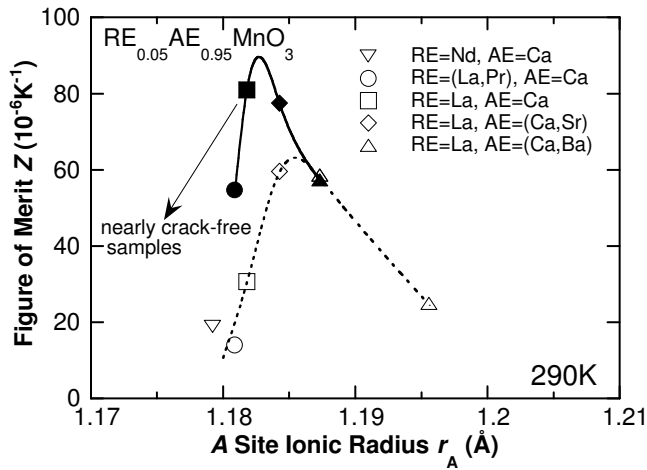
Fig. 2 shows the average A-site ionic radius ( $r_A$ ) dependence of (a) the resistivity  $\rho$  and Seebeck coefficient  $S$  and (b) the thermal conductivity  $\kappa$  and figure of merit  $Z$  for various  $\text{RE}_{0.10}\text{AE}_{0.90}\text{MnO}_3$  samples at 290 K. The  $\rho$  values decrease with increasing  $r_A$  for  $\text{RE}_{0.10}\text{Ca}_{0.90}\text{MnO}_3$  and then takes a minimum at  $r_A=1.184\text{\AA}$  (RE=La) and increases with further increase of  $r_A$  for the  $\text{La}_{0.10}(\text{Ca}_{1-Z}\text{Sr}_Z)_{0.90}\text{O}_3$  system. The temperature dependence of  $\rho$  is semiconductive, *i.e.*,  $\rho$

increases with decreasing  $T$  for all the samples in this study. The  $S$  value hardly depends on  $r_A$  and the  $\kappa$  value slightly decreases with increasing  $r_A$ . The increase of  $r_A$  results in the reduction of the static lattice distortion from the cubic structure with the tolerance factor  $\Gamma$  approaching 1 as shown in the upper axis of abscissas. The  $\rho$  reduction in  $\text{RE}_{0.10}\text{Ca}_{0.90}\text{MnO}_3$  may result from the decrease in the lattice distortion from the cubic, originating from the broadening of the bandwidth. The  $\rho$  increase for  $r_A>1.184\text{\AA}$  may come from the introduction of the lattice disorder and/or the increase of the radius variance  $\sigma^2$  caused by the substitution of Sr for the Ca-site.

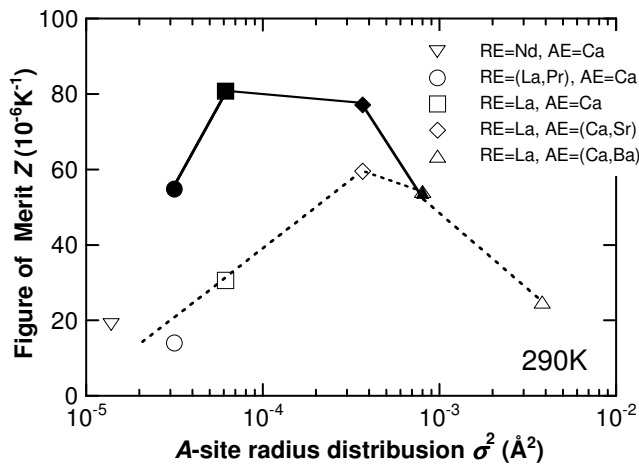
The similar  $r_A$  dependences can be seen for the 5% electron doping system. Fig. 3 shows (a) the resistivity  $\rho$ , (b) the Seebeck coefficient  $S$  and (c) the thermal conductivity  $\kappa$  for  $(\text{RE}_{0.05}\text{AE}_{0.95})\text{MnO}_3$  samples at 290 K as a function of  $r_A$ . In these figures, the bold symbols show the values of which the samples were carefully cut from the nearly crack-free region of the sintered pellets. For the majority samples bearing some cracks as shown in the open symbols, the  $\rho$  value takes a minimum and the  $S$  value takes a faint maximum around  $r_A\sim 1.183\text{\AA}$  for  $\text{La}_{0.05}(\text{Ca}_{0.98}\text{Sr}_{0.02})_{0.95}\text{MnO}_3$ . The  $\kappa$  value slightly decreases with increasing  $r_A$ . These behaviors are similar to those for the  $\text{RE}_{0.10}\text{AE}_{0.90}\text{MnO}_3$  shown in Fig. 2. For the nearly crack-free samples, the low  $\rho$  value and the high  $\kappa$  value are naturally expected. The extremely strong enhancement in the  $S$  value was observed for the  $\text{La}_{0.05}(\text{Ca}_{0.98}\text{Sr}_{0.02})_{0.95}\text{O}_3$  and  $\text{La}_{0.05}\text{Ca}_{0.95}\text{MnO}_3$  samples. One possible explanation is that the intrinsic higher TE potential was masked out by the existence of the cracks.



**Figure 3:** The  $r_A$  dependence of (a)  $\rho$ , (b)  $S$  and (c)  $\kappa$  for  $\text{RE}_{0.05}\text{AE}_{0.95}\text{MnO}_3$  at 290 K.



**Figure 4:** The  $r_A$  dependence of  $Z$  for  $\text{RE}_{0.05}\text{AE}_{0.95}\text{MnO}_3$  at 290 K.

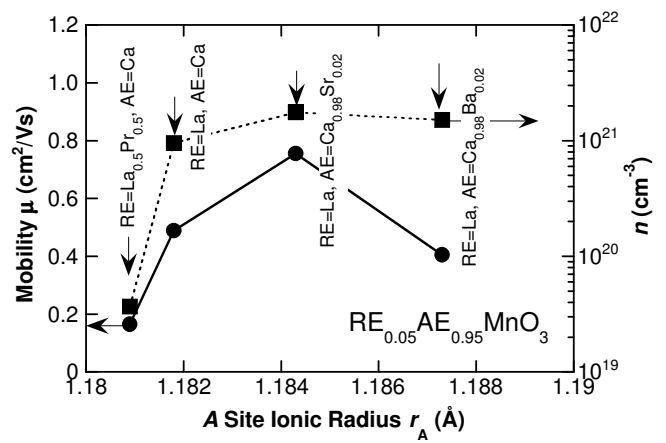


**Figure 5:** The  $Z$  value for the  $\text{RE}_{0.05}\text{AE}_{0.95}\text{MnO}_3$  samples at 290 K as a function of  $\sigma^2$ .

Fig. 4 shows the figure of merit  $Z$  as a function of  $r_A$  for  $\text{RE}_{0.05}\text{AE}_{0.95}\text{MnO}_3$  samples at 290 K. For both the crack-bearing and nearly crack-free samples, the  $Z$  value takes a maximum around  $r_A=1.812\sim 1.814$  Å, depending on the  $r_A$  value. The  $Z$  value obtained in this study was lower than the reported values of  $\text{Bi}_{0.04}\text{Ca}_{0.96}\text{MnO}_3$  ( $Z=98 \times 10^{-6} \text{ K}^{-1}$ ) [7] and  $\text{Bi}_{0.10}\text{Ca}_{0.90}\text{MnO}_3$  ( $Z=350 \times 10^{-6} \text{ K}^{-1}$ ) [4].

Fig. 5 shows the  $Z$  value for  $\text{RE}_{0.05}\text{AE}_{0.95}\text{MnO}_3$  at 290 K as a function of the A-site ionic radius distribution (variance)  $\sigma^2$ . The  $Z$  value takes a maximum and then decreases with increasing  $\sigma^2$ . The increase of  $\sigma^2$  indicates the increase of the A-site lattice randomness in the perovskite structure. In Fig. 4, the  $Z$  increase with increasing  $r_A$  for  $r_A < 1.184$  Å may result from the decrease in the lattice distortion and the  $Z$  decrease for  $r_A > 1.184$  Å may result from the increase of  $\sigma^2$  and/or the introduction of the crystal disorder caused by the substitution by Sr or Ba ions for the Ca-site.

Fig. 6 shows the mobility  $\mu$  and the carrier concentration  $n$  for the  $\text{RE}_{0.05}\text{AE}_{0.95}\text{MnO}_3$  samples at 290 K as a function of  $r_A$ , which were estimated by the Hall coefficient. The mobility  $\mu$  shows a maximum at  $r_A \sim 1.184$  Å, where the  $\rho$



**Figure 6:** The mobility  $\mu$  and the carrier concentration  $n$  for  $\text{RE}_{0.05}\text{AE}_{0.95}\text{MnO}_3$  at 290 K as a function of  $r_A$ .

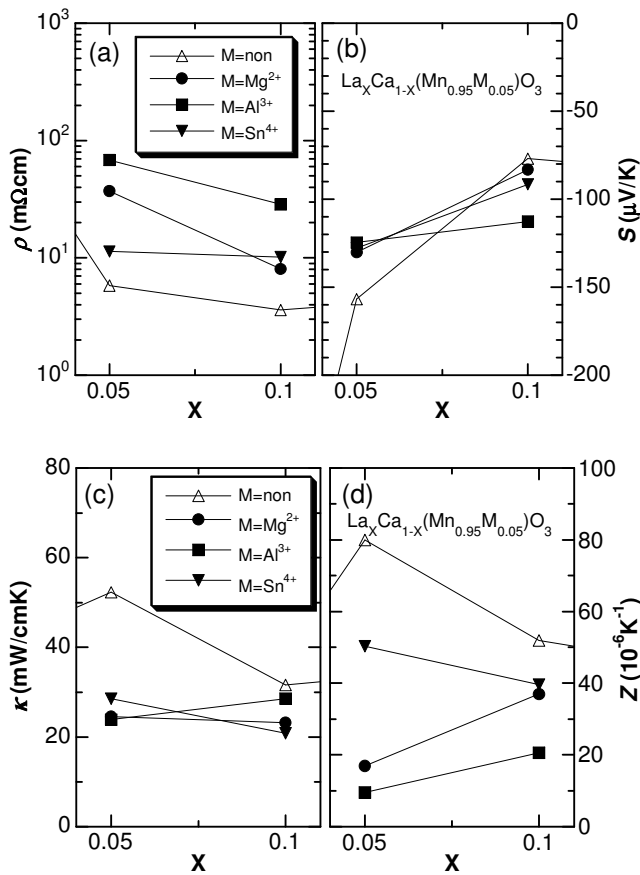
shows a lower value shown in Fig. 3(a). The  $n$  value, at which  $Z$  takes a maximum, is  $1 \times 10^{21} \text{ cm}^{-3}$  and these results indicate that the carrier hopping is the main conduction mechanism in this system. However, it must be noted that only the average radius  $r_A$  is not the main factor to determine  $\mu$  and  $\sigma$  ( $=1/\rho$ ) as clarified the maximum at  $r_A \sim 1.184$  Å.

### 3.2 $\text{La}_x\text{Ca}_{1-x}(\text{Mn}_{0.95}\text{M}_{0.05})\text{O}_3$ system ( $X=0.05, 0.10$ )

We have investigated the effect of the Co-site substitution by the various elements on the TE properties for  $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{1-z}\text{M}_z)\text{O}_3$  [8,9]. It was found that the ionic valency of the substituted element  $M$  more strongly influenced the thermoelectricity rather than the ionic radius or spin state of the element  $M$ . The valence effect of the dopants for the Mn-site substitution on the TE properties were studied for  $\text{La}_x\text{Ca}_{1-x}(\text{Mn}_{0.95}\text{M}_{0.05})\text{O}_3$  ( $X=0.05, 0.10$ ;  $M=\text{Mg}^{2+}, \text{Al}^{3+}, \text{Sn}^{4+}$ ). The substitution by the 2+ ions ( $\text{Mg}^{2+}$ ) is expected to make the average Mn valency increase and the substitution by the 4+ ions ( $\text{Sn}^{4+}$ ) is expected to make the average Mn valency slightly decrease. Fig. 7 shows (a) the resistivity  $\rho$ , (b) the Seebeck coefficient  $S$ , (c) the thermal conductivity  $\kappa$  and (d) the figure of merit  $Z$  for  $\text{La}_x\text{Ca}_{1-x}(\text{Mn}_{0.95}\text{M}_{0.05})\text{O}_3$  ( $X=0.05, 0.10$ ) at 290 K. The  $\rho$  values increase and the  $\kappa$  values decrease for the Mn-site substitution owing to the introduction of the disorder in the  $\text{MnO}_6$  network. The  $\rho$  values for the  $\text{Al}^{3+}$  substitution are the largest and are about an order of magnitude higher than those of the non-substituted samples. The absolute values of  $S$  slightly increase by the Mn-site substitution for  $X=0.10$ , but decrease for  $X=0.05$ . As a result, the  $Z$  value decreases by the Mn-site substitution for both  $X=0.05$  and 0.10 samples relative to the non-substituted  $\text{La}_x\text{Ca}_{1-x}\text{MnO}_3$ . The Mn-site substitution seriously damages the TE properties irrespective of the ionic valency of the substituted elements in contrast with the  $\text{La}_{0.80}\text{Sr}_{0.20}(\text{Co}_{1-z}\text{M}_z)\text{O}_3$  system.

## 4. Conclusions

The thermoelectric (TE) properties of the electron-doped ( $\text{RE}_x\text{AE}_{1-x}$ ) $\text{MnO}_3$  ( $X=0.05, 0.10$ ) have been investigated as a



**Figure 7:** The X dependence of (a)  $\rho$ , (b)  $S$ , (c)  $\kappa$  and (d)  $Z$  of  $\text{La}_x\text{Ca}_{1-x}(\text{Mn}_{0.95}\text{M}_{0.05})\text{O}_3$  at 290 K ( $M=\text{Mg}^{2+}, \text{Al}^{3+}, \text{Sn}^{4+}$ ).

function of the average ionic radius  $r_A$  of the A-site cation in the perovskite structure. The electrical resistivity  $\rho$ , Seebeck coefficient  $S$  and the thermal conductivity  $\kappa$  have been measured and the figure of merit  $Z$  and the power factor  $P$  have been estimated. Important experimental results and conclusions obtained in this study are summarized as follows.

- (1) The  $\rho$ ,  $S$  and  $\kappa$  values depend on  $r_A$ . Near the room temperature, the  $Z$  value shows a maximum at  $r_{A(\text{opt})}=1.182\sim 1.184\text{\AA}$ , which is realized for the  $\text{La}_{0.10}\text{Ca}_{0.90}\text{MnO}_3$  and  $\text{La}_{0.05}(\text{Ca}_{0.98}\text{Sr}_{0.02})_{0.95}\text{MnO}_3$ . The decrease of  $Z$  with decreasing  $r_A$  from  $1.182\text{\AA}$  may result from the decrease of the tolerance factor  $T$  and the decrease of  $Z$  with increasing  $r_A$  from  $1.184\text{\AA}$  may result from the introduction of the crystal disorder and/or the increase of the radius variance  $\sigma^2$ . The  $P$  value shows the similar  $r_A$  dependence.
- (2) The 5% substitution by elements M for the Mn-site degrades the TE properties in  $\text{La}_x\text{Ca}_{1-x}(\text{Mn}_{0.95}\text{M}_{0.05})\text{O}_3$  ( $X=0.05, 0.10$ ) compared with the non-substituted samples. The TE property degradation of this system is mainly caused by the crystal disorder in the  $\text{MnO}_6$  network and is nearly independent of the ionic valency of the substituted elements.
- (3) The cracks, inevitably induced in the samples during the sintering process, seriously reduce the TE properties especially for the small X region ( $0\leq X\leq 0.10$ ).

## Acknowledgments

This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of the Education, Culture, Sports, Science and Technology, Japan (No. 14550661). This work was partially performed under the interuniversity cooperative research program of the Institute for Materials Research, Tohoku University (Prof. T. Goto), and under the Japan-Czech Republic Cooperative Research Project in 2003.

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