Seebeck coefficient of Ln$_x$Ca$_{1-x}$MnO$_3$ perovskites in paramagnetic state

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Received: 3 May 2010 / Accepted: 11 October 2010 / Published online: 21 October 2010 © Springer-Verlag 2010

Abstract The Seebeck coefficient is a function of carrier concentration and configurational entropy. In this report, we semi-theoretically investigate the Seebeck coefficient of Ln$_x$Ca$_{1-x}$MnO$_3$ (Ln = Rare-earth) perovskites based on the electronic structure of the 3$d$ orbitals of Mn ions, using the developed Heikes model, Boltzmann transport model, and diffusion model. The results show that the Seebeck coefficient of such a strongly correlated electron system in paramagnetic state is remarkably affected by site degeneracy. As temperature decreases, the evolution of the spin and orbital degrees of freedom together with the change in phonon scattering mode describes the Seebeck coefficient behavior satisfactorily. The phonon drag effect at low temperature is also discussed.

1 Introduction

Seebeck and Peltier effects relative to thermoelectricity are fundamental thermodynamic phenomena which can offer solid-state refrigeration and electrical power generation [1, 2]. To make devices based on Seebeck and Peltier effects, a major challenge is to find materials with efficient thermoelectric performance. The thermoelectric efficiency of materials is usually expressed by the figure of merit $Z$ (defined as $Z = S^2 / \rho \kappa$, where $S$, $\rho$, and $\kappa$ are Seebeck coefficient, resistivity, and thermal conductivity, respectively). So far, alloyed semiconductors have mostly been used as thermoelectric materials due to their higher figure of merit. Compared with the traditional thermoelectric alloys, metal oxides as a new category of thermoelectric materials have many peculiar advantages such as chemical stability, oxidation resistance, easy manufacture, and low-cost. Over the decade, since the discovery of large Seebeck coefficient in the layered oxide NaCo$_2$O$_4$ [3], there has been a growing interest in the study on oxide thermoelectric materials. In succession, it has been found that some other strongly correlated electron systems, for instance, titanates, cobaltites, and manganites, also exhibit good thermoelectric characteristics [4–7]. In these 3$d$ transition-metal oxides, a heavy effective mass of carriers due to the strong electronic correlation is believed to be responsible for the large Seebeck coefficient [2, 8]. On the other hand, spin and orbital degeneracies, which usually exist in transition-metal oxides, have been proposed to produce extra thermoelectric power [9]. In fact, some transition-metal oxides such as SrTiO$_3$ and NaCo$_2$O$_4$ have been demonstrated to be associated with spin degeneracy or orbital degeneracy [4, 10]. This can partially explain the source of good thermoelectric performance in these metal oxides.

Among the 3$d$ transition-metal oxides as mentioned above, perovskite manganites Ln$_x$A$_{1-x}$MnO$_3$ (Ln = rare-earth, A = alkaline-earth) exhibit not only good thermoelectric response, but also rich magnetic and transport properties, such as colossal magnetoresistance (CMR) effect, spin...
glass behavior, and magnetic phase separation [11–16]. In contrast to the widely-investigated resistivity, susceptibility, and specific heat, etc., the Seebeck coefficient of this system has not been investigated in detail to our knowledge [17–19]. Although some theoretical studies were carried out [20–22], the fact is that these theories cannot account well for the Seebeck coefficient behavior in manganite systems [23]. Actually, in the manganite perovskites, the \( t_{2g} \) orbitals with lower energy are filled and do not participate directly in transport process, but they can contribute to the overall spin degeneracy of Mn sites and thus contribute to Seebeck coefficient [22]. Furthermore, there may exist several cases for the relationship among Jahn-Teller splitting energy of Mn sites, Coulomb interactions, and thermal energy of electrons. This will yield various spin and orbital degeneracies. Therefore, the description of Seebeck coefficient of manganese oxides is quite complicated. Systematic investigations combining theories and experiments on this topic remain scanty.

In this study, we focus on the Seebeck coefficient of electron-doped \( \text{Ln}_{x}\text{Ca}_{1-x}\text{MnO}_3 \) series from low temperature up to 1000 K, in order to explore the source of the anomalous Seebeck coefficient in this system. The analysis presented here is helpful for the understanding of the structure, electrical, magnetic properties of manganite perovskites and the search of new thermoelectric oxides with high performance.

### 2 Experimental

\( \text{Ln}_{x}\text{Ca}_{1-x}\text{MnO}_3 \) ceramics were prepared by a conventional solid-state reaction. High-temperature resistivity and Seebeck coefficient were measured by using SourceMeter (KEITHLEY) and 2000 Multimeter (KEITHLEY), respectively, while high-temperature thermal conductivity data were collected by measuring specific heat capacity, thermal diffusivity (Netzsch LFA-427), and material density. The detailed synthesis method and the measurements for high-temperature thermal conductivity were reported elsewhere [24]. X-ray diffraction (XRD) data, collected by using Bede D1 XRD diffractometer, confirmed that all the samples are single-phase with an orthorhombic-perovskite structure. Iodometric titration and thermogravimetric analysis (TGA) indicated that the oxygen stoichiometry for all samples is equal to 3.00 ± 0.01. The TGA results also indicated that there is no oxygen volatilization from room temperature up to 1000 K, so the high-temperature resistivity and Seebeck coefficient measurements were performed in air and ambient pressure. The high-temperature resistivity and Seebeck coefficient of several samples were also measured by using a different equipment (ULVAC-RIKO ZEM-3) and in a low vacuum He atmosphere. The data obtained from the two equipments are identical and well reproducible. In the temperature range from 5 to 300 K, Seebeck coefficient, specific heat, and thermal conductivity were all measured by using the Quantum Design physical property measurement system (PPMS).

### 3 Results and discussion

As electron-doped \( \text{CaMnO}_3 \) families show good thermoelectric characteristics [24, 25], some all-oxide thermoelectric power generators have been fabricated by using rare-earth doped \( \text{CaMnO}_3 \) in an electron-doped range as \( n \)-type legs [26, 27]. The thermoelectric performance of this system depends strongly on doped ions and doping level [25, 28–30]. To obtain the optimal doping content in these rare-earth doped \( \text{CaMnO}_3 \), recently we systematically investigated the high-temperature thermoelectric response in electron-doped \( \text{CaMnO}_3 \), and we found that \( \text{Ln}_x\text{Ca}_{1-x}\text{MnO}_3 \) at \( x \sim 0.1 \) exhibits the best thermoelectric properties [30]. As shown in Fig. 1, with the increase in rare-earth content in each series, the resistivity \( \rho \) first decreases, reaches a minimum, and then increases, while both the absolute value of Seebeck coefficient \( |S| \) and the thermal conductivity \( \kappa \) monotonously decreases. As a result, the largest power factor \( P \) (defined by \( P = S^2/\rho \)) along with the highest \( ZT \) value occurs at the doping level of \( x = 0.1 \). This is mainly because of the relatively low \( \rho \) and moderate \( S \) and \( \kappa \) in the \( \text{Ln}_0\text{Ca}_{0.9}\text{MnO}_3 \) specimens. Although the decrease in \( |S| \) with doping may be attributed to the increase in electron concentration [29], \( S \) cannot be quantitatively determined only by the electron concentration, whereas the spin and/or orbital degeneracy also play an important role [22]. The intrinsic reason why the optimal \( ZT \) always exists in these \( x = 0.1 \) samples remains puzzling, but the \( \text{Ln}_0\text{Ca}_{0.9}\text{MnO}_3 \) specimens do exhibit an applicable potential. In a view of the applicable aspect, next we focus mainly on the \( x = 0.1 \) doped samples with good performance and analyze their Seebeck coefficient behavior.

Figure 2 presents the temperature dependence of \( S \) for \( \text{Ln}_0\text{Ca}_{0.9}\text{MnO}_3 \) from 5 up to 1000 K. The \( S \) data in the two temperature regions, 5–300 K and 300–1000 K, were obtained from different measurement apparatuses, so the \( S-T \) plots cannot change smoothly at 300 K. The values of \( S \) for all samples are negative, indicating the nature of electron conduction (i.e. \( n \)-type). In addition, these samples have identical electron concentration and electronic configuration, so they exhibit almost same \( S \) values. The slight difference of \( S \) might originate from the different structural distortions, since structural distortions can influence exchange integral and bandwidth [31].

As temperature decreases, \( S \) undergoes the following evolutions: from 1000 to \( \sim \)700 K, \( S \) keeps nearly unchanged; from \( \sim \)700 to \( \sim \)220 K, \( S \) monotonously decreases with the reduction in \( T \); in the range of 220–100 K, \( S \) shows a hump; around \( \sim \)100 K, \( S \) sharply drops.