THERMAL TRANSPORT IN FERROMAGNETIC La$_{1-x}$AE$_x$MnO$_3$ WITH LARGE DIVALENT IONS*

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The thermal conductivity $\kappa(T)$ of the La$_{1-x}$AE$_x$MnO$_3$ manganites (AE: divalent ions, Ca$^{2+}$, Sr$^{2+}$, Pb$^{2+}$, Ba$^{2+}$) has been measured. For small AE ions (Ca$^{2+}$ and Sr$^{2+}$), $\kappa(T)$, which is dominated by the phonon contribution, shows an enhancement below the ferromagnetic transition temperature $T_c$. In contrast, the enhancement is completely wiped out for the largest Ba$^{2+}$ ion. The increase of the ionic radius of AE ions reduces the average static lattice distortion with the tolerance factor $\tau$ approaching 1, while it increases the randomness of ionic radii in the (La$_{1-x}$AE$_x$)-site cations defined by the cation radius variance $\sigma^2$. In the Ba$^{2+}$ system, the $\kappa(T)$ reduction caused by the largest $\sigma^2$ masks the $\kappa(T)$ enhancement characteristic of the ferromagnetic-metal manganite systems.

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1. Introduction

As recently revived studies on perovskite-based manganese have confirmed, (RE$_{1-x}$AE$_x$)MnO$_3$-type crystals (RE= trivalent rare-earth ions such as La$^{3+}$, Pr$^{3+}$; AE= divalent ions such as Ca$^{2+}$, Sr$^{2+}$) undergo a variety of dramatic phenomena such as the colossal magnetoresistance (CMR) and the insulator-metal (I-M) transition [1], etc. The phonon thermal conductivity $\kappa_{ph}(T)$ is a valuable tool to investigate the effect of the lattice dynamics on the phase transitions of the manganite system [2, 3]. In the La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) system, for example, the thermal conductivity $\kappa(T)$ increases abruptly below the ferromagnetic metal (FM-M) transition temperature $T_c$ for 0.19$\leq x \leq$0.30 [4]. The increase of the AE-ion radius $(r_{AE})$ in the ABO$_3$ perovskite manganites results in the reduction of the static lattice distortion from the cubic structure with the tolerance factor

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\( \Gamma = (r_A + r_0)/(\sqrt{2}(r_B + r_0)) \) approaching 1, where \( r_A \), \( r_B \) and \( r_0 \) are the atomic radii of \( A \)-site (\( \text{La}^{3+} \)) ion, \( B \)-site (\( \text{Mn}^{3+} \)) ion and oxygen, respectively. The \( \Gamma \) value affects the \( T_c \) value through the one electron bandwidth \( W \) and the widened \( W \) enhances \( T_c \) as the lattice approaches to cubic. On the other hand, \( T_c \) also depends on the size differences within the \( A \)-site (\( \text{La}^{3+} \) and \( \text{AE}^{2+} \)) cations, even if \( \Gamma \) is kept constant [5]. The randomness of the \( A \)-site cations is defined by the \( A \)-site cation variance \( \sigma^2 = \sum y_i r_i^2 - r_0^2 \), \( y_i \) is the fractional occupancy of the \( A \)-site species and \( r_A \) is the average ionic radius of \( A \)-site cations) and \( \sigma^2 \) increases with increasing \( \text{AE} \)-site ionic radius in the present \( \text{La} \)-based manganites. In this paper, \( \kappa(T) \) of \( \text{La}_{1-X}\text{AE}_X \text{MnO}_3 \) is studied for various sizes of the \( \text{AE} \) ions. We discuss the origin of the \( \kappa(T) \) anomalies below \( T_c \) from the point of view of the lattice distortions.

2. Experimental

\( \text{La}_{1-X}\text{AE}_X \text{MnO}_3 \) samples (\( \text{AE} = \text{Ba}^{2+}, \text{Pb}^{2+}, \text{Sr}^{2+}, \text{Ca}^{2+} \)) were prepared by a solid-state reaction method for the hole concentration \( X = 0.1 \sim 0.5 \). The sizes of \( r_{AE} \) are \( r(\text{Ca}^{2+}) < r(\text{Sr}^{2+}) < r(\text{Pb}^{2+}) < r(\text{Ba}^{2+}) \) and \( \Gamma \) and \( \sigma^2 \) were calculated using the tabulated radii with ninefold coordination [6]. The samples were fabricated by solid state reaction method at 1500°C for 8 h in air [4, 8]. The grain size of each sample is about 10 \sim 20 \mu m and is independent of the species of \( \text{AE} \) ions and the hole concentration \( X \). The thermal conductivity \( \kappa(T) \) was measured by a steady-state heat flow method using a Gifford–McMahon (GM) cycle helium refrigerator as a cryostat.

3. Results and discussion

Figure 1 shows \( \kappa(T) \) of \( \text{La}_{1-X}\text{AE}_X \text{MnO}_3 \) samples ((a) \( X = 0.20 \) and (b) \( X = 0.30 \)). All the samples show the metallic electrical conduction below the FM-M transition temperature \( T_c \) [4, 7, 8]. For \( X = 0.20, \kappa(T) \) of the \( \text{Ca}^{2+}, \text{Sr}^{2+} \) and \( \text{Pb}^{2+} \) systems, which is overwhelmingly due to the phonon contribution, shows a characteristic enhancement below \( T_c \) (=200 K for \( \text{AE} = \text{Ca}^{2+} \) and =330 K for \( \text{AE} = \text{Sr}^{2+} \)) and then reaches a maximum at around \( T \approx \)40 K. These anomalous temperature dependences are considered to result from the reduction in the phonon scattering related to the relaxation of the spatially random Jahn–Teller (J–T) distortion in the metallic phase. With initial increase of \( r_{AE} \) from \( \text{AE} = \text{Ca}^{2+} \) to \( \text{AE} = \text{Sr}^{2+} \), the absolute values of \( \kappa(T) \) remarkably increases, which suggests that the increase of \( r_{AE} \) enhances the phonon thermal conduction possibly by reducing the lattice distortion from cubic. It is to be noticed that the crystal structure is orthorhombic for LCMO and changes to rhombohedral for the
La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) system. With further increase of $r_{AE}$, however, the absolute value of $\kappa(T)$ is reduced significantly. For the Ba$^{2+}$ system (LBMO) with the largest $r_{AE}$, $\kappa(T)$ monotonically decreases with the decrease in temperature. For $X = 0.30$ shown in Fig. 1(b), the $\kappa(T)$ maximum at low temperatures is enhanced for LCMO and LSMO, but it is strongly suppressed for the Pb$^{2+}$ system (LPMO). A comparison of high temperature $\kappa(T)$ around 300 K for $X = 0.20$ and $X = 0.30$ shows that $\kappa(T)$ values of LPMO and LBMO are somewhat enhanced with increasing $X$. This enhancement is far clearer for LBMO, which may suggest that the $\kappa$ enhancing effect related to increasing $\Gamma$ is still at work in these two systems at the high temperatures [8].

![Thermal Conductivity](image)

**Fig. 1.** Thermal conductivity $\kappa(T)$ of La$_{1-x}$AE$_x$MnO$_3$ ((a): $X = 0.20$, (b): $X = 0.30$) for various sizes of AE ions. Arrows show $T_c$ which was magnetically determined.

Figure 2 presents the calculated values of (a) $\Gamma$ and (b) $\sigma^2$, as a function of the hole concentration $X$. $\Gamma$ increases with increasing $X$ and with increasing $r_{AE}$, which may tend to bring about the $\kappa(T)$ enhancement. On the other hand, $\sigma^2$, the randomness of the $A$-site cations, also increases with increasing $X$ and $r_{AE}$. The increase in $\sigma^2$ corresponds to an increase of the randomness of the local lattice distortion and should reduce $\kappa(T)$. In Fig. 1, $\kappa(T)$ of LBMO is smaller than those of other systems at low temperatures. This result suggests that the reduction mechanism due to the large $\sigma^2$ value is very strong in the Ba$^{2+}$ system especially at low temperatures. least at low temperatures.
Fig. 2. Calculated values of (a) tolerance factor $\Gamma$ and (b) cation radius variance $\sigma^2$ as a function of hole concentration $X$.

In summary, the increase of the AE ion radius brings about both enhancing and reducing effects on the phonon thermal conductivity. In the Ba$^{2+}$ system with the largest AE ion radius, the effect of the $\kappa(T)$ reduction due to the large $\sigma^2$ values may be more dominant than the $\kappa(T)$ enhancing effect due to the large $\Gamma$ value. In the Pb$^{2+}$ system, the reduction effect seems to be dominant at low temperatures.

REFERENCES