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THERMAL TRANSPORT IN FERROMAGNETIC $La_{1-X}AE_XMnO_3$ WITH LARGE DIVALENT IONS*

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The thermal conductivity $\kappa(T)$ of the $La_{1-X}AE_XMnO_3$ 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 metal 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 Γ approaching to 1, while it increases the randomness of ionic radii in the $(La_{1-X}AE_X)$-site cations defined by the cation radius variance σ^2. In the Ba^{2+} system, the $\kappa(T)$ reduction caused by the largest σ^2 masks out 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 $\kappa_{\mathrm{ph}}(T)$ is a valuable tool to investigate the effect of the lattice dynamics on the phase transitions of the manganite system [2, 3]. In the $La_{1-X}Ca_XMnO_3$ (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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Γ ($=(r_A+r_O)/(\sqrt{2}(r_B+r_O))$) approaching 1, where r_A, r_B and r_O are the atomic radii of A-site ($La_{1-X}AE_X$) ion, B-site ($Mn^{3+}{}_{1-X}Mn^{4+}{}_X$) ion and oxygen, respectively. The Γ 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 (La^{3+} and AE^{2+}) cations, even if Γ is kept constant [5]. The randomness of the A-site cations is defined by the A-site cation radius variance σ^2 ($=\Sigma y_i r_i^2$-r_A^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 σ^2 increases with increasing AE-site ionic radius in the present La-based manganites. In this paper, $\kappa(T)$ of $La_{1-X}AE_XMnO_3$ is studied for various sizes of the 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

$La_{1-X}AE_XMnO_3$ samples (AE=Ba^{2+}, Pb^{2+}, Sr^{2+}, 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 $r(Ca^{2+})<r(Sr^{2+})<r(Pb^{2+})<r(Ba^{2+})$ and Γ and σ^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 $10 \sim 20$ μm and is independent of the species of 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 $La_{1-X}AE_XMnO_3$ 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 Ca^{2+}, Sr^{2+} and Pb^{2+} systems, which is overwhelmingly due to the phonon contribution, shows a characteristic enhancement below T_c (=200 K for AE = Ca^{2+} and = 330 K for AE = Sr^{2+}) and then reaches a maximum at around $T\simeq 40$ 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 AE = Ca^{2+} to AE = 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

$La_{1-X}Sr_XMnO_3$ (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 κ enhancing effect related to increasing Γ is still at work in these two systems at the high temperatures [8].

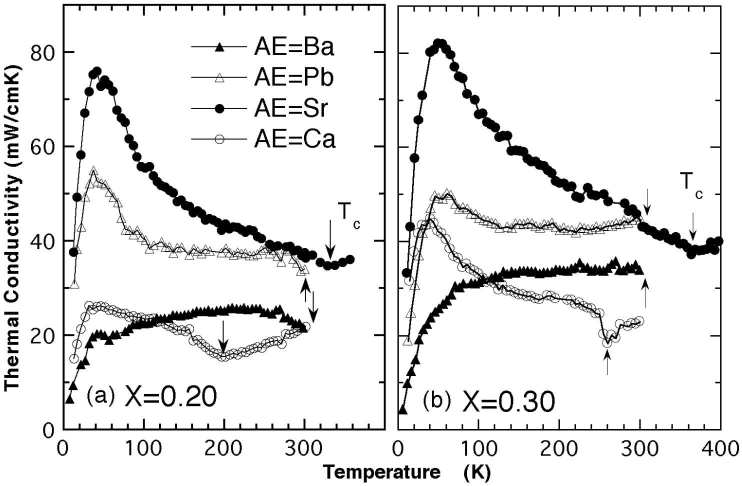

Fig. 1. Thermal conductivity $\kappa(T)$ of $La_{1-X}AE_XMnO_3$ ((a): $X = 0.20$, (b): $X = 0.30$) for various sizes of AE ions. Arrows show T_c which was magnetically determined.

Figure 2 presents the calculated values of (a) Γ and (b) σ^2, as a function of the hole concentration X. Γ increases with increasing X and with increasing r_{AE}, which may tend to bring about the $\kappa(T)$ enhancement. On the other hand, σ^2, the randomness of the A-site cations, also increases with increasing X and r_{AE}. The increase in σ^2 corresponds to the 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 σ^2 value is very strong in the Ba^{2+} system especially at low temperatures. least at low temperatures.

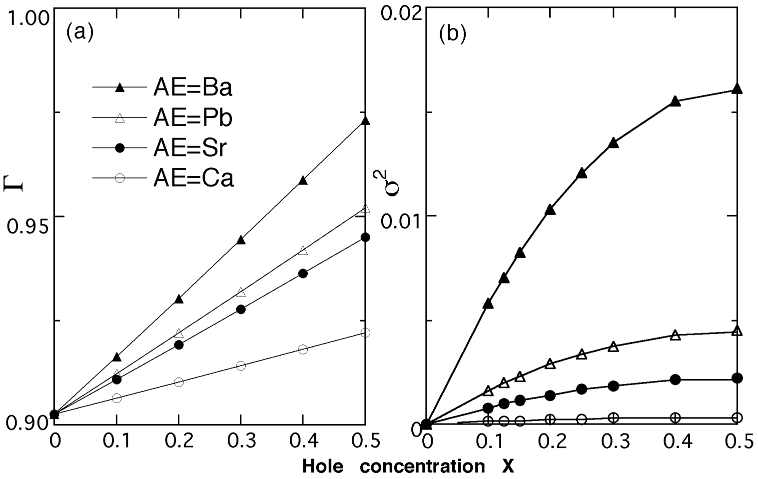

Fig. 2. Calculated values of (a) tolerance factor Γ and (b) cation radius variance σ^2 as a function of hole concentration X.

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 σ^2 values may be more dominant than the $\kappa(T)$ enhancing effect due to the large Γ value. In the Pb^{2+} system, the reduction effect seems to be dominant at low temperatures.

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