Analysis of Relationship between Dynamic Interlayer Interactions and Phonon Thermal Conduction in $Ca_3Co_4O_9$

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The layered cobalt oxides such as $Ca_3Co_4O_9$ [1] have attracted great attention as candidates for p-type thermoelectric materials due to their high power factor like metal and low thermal conductivity as ceramics. These crystal structures consist of CdI_2-type CoO_2 layer sandwiching another layer and they are thermodynamically stable. Origins of electronic properties in these materials have been extensively studied, and it is well known that their electronic properties are originated from electron correlation of cobalt in CoO_2 layer [2],[3]. In contrast, understandings of thermal properties, especially their low thermal conductivity, are generally very limited simply because conventional theories of thermal conduction are of little use for oxides. Earlier computational studies of thermal conduction in Na_xCoO_2, which is the most well-known layered cobaltite, revealed that point defects in Na layers sandwiched by CoO_2 layers trigger phonon scattering in the CoO_2 layers and reduce overall thermal conductivity [4]. These facts indicate interesting possibility that properties in one layer can be altered indirectly and selectively by controlling the other layer, which provides more degrees of freedom to optimize thermoelectric properties. However, it is still unclear that what governs thermal conduction in misfit layered $Ca_3Co_4O_9$, just because its crystal structure, in which two dissimilar layers stacking alternately as shown in Fig. 1, is more complicated and many factors affect its thermal conduction. It makes difficult materials designing for better thermoelectric properties.

In this study, various computational experiments have been carried out in order to reveal the atomistic mechanism of thermal conduction in $Ca_3Co_4O_9$ and other layered cobaltites, and to acquire strategies to improve thermoelectric properties in these materials from the point of view of thermal conduction. Phonon thermal conductivity in layered cobaltites was obtained by perturbed molecular dynamics calculation [5]. In this method, atomic interactions were described with an empirical pair-wise potential set using Buckingham function.

Phonon thermal conductivities of $Ca_3Co_4O_9$ and $Ca_{0.25}CoO_2$, which is non-misfit layered cobaltites composed of the same set of elements as $Ca_3Co_4O_9$, were shown in Fig. 2. Through comparisons between the two layered calcium cobaltites, it is found that phonon thermal conductivity of CoO_2 layer is lower in $Ca_3Co_4O_9$ than $Ca_{0.25}CoO_2$, due to more distorted local coordination of CoO_2 octahedra caused primarily by structural misfit between two dissimilar layers. In $Ca_{0.25}CoO_2$, most of heat is transported through CoO_2 layer. By contrast, in $Ca_3Co_4O_9$, CoO_2 layer and rock salt type Ca_2CoO_3 layer transports almost 70% and 30% of heat energy respectively. This result means that disturbing thermal conduction in both layers simultaneously is important to reduce overall thermal conductivity of $Ca_3Co_4O_9$. Detailed analyses, in which distortion in $Ca_3Co_4O_9$ is artificially changed, indicate that low thermal conductivity of $Ca_3Co_4O_9$ is originated not only from structural misfit but also from

dynamic interlayer interaction between CoO_2 layer and Ca_2CoO_3 layer [6]. This is confirmed by independent computational experiments where only dynamic interlayer interaction is intentionally changed. Furthermore, additional computational experiments, in which some Ca in Ca_2CoO_3 layer substituted by Sr, was performed. Phonon thermal conductivities of $Ca_3Co_4O_9$, Sr15%-doped $Ca_3Co_4O_9$, and $Sr_3Co_4O_9$ were shown in Table 1. It is found that phonon thermal conductivity of $Sr_3Co_4O_9$ is higher than $Ca_3Co_4O_9$, although Sr is heavier than Ca. By comparison of undulation of CoO_2 layer, $Sr_3Co_4O_9$ has less distorted structure than $Ca_3Co_4O_9$ and it is considered that this causes higher thermal conductivity of $Sr_3Co_4O_9$. On the other hand, in Sr-doped $Ca_3Co_4O_9$, it is found that not only local thermal conductivity of Ca_2CoO_3 layer but also that of CoO_2 layer were suppressed, although undulation of CoO_2 layer was relaxed by substituting of Sr for Ca. This result is associated with the effect of dynamic interlayer interaction, and suggests a way to further improve thermal properties of CoO_2 layer indirectly without deteriorating its electronic properties, by controlling Ca_2CoO_3 layer.

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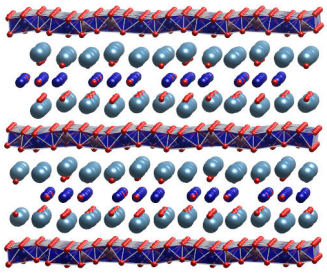
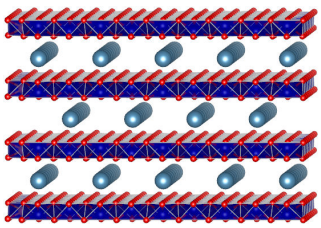
References: [1] R. Funahashi, et al., *Jpn. J. Appl. Phys.*, **39**(2000), L1127. [2] D. J. Singh, *Phys. Rev. B*, **61**(2000), 13397. [3] W. Koshibae, et al., *Phys. Rev. B*, **62**(2000), 6869. [4] M. Tada, et al., *J. Electron. Mater.*, **39**(2010), 1439. [5] M. Yoshiya, et al., *Mol. Simulat.*, **30**(2004), 953. [6] S. Fujii, et al., *J. Electron. Mater.*, published on-line: DOI:10.1007/s11664-013-2902-7



(a) $Ca_3Co_4O_9$



(b) $Ca_{0.25}CoO_2$

FIG. 1. Crystal structure of two layered calcium cobaltites. Red, light-blue, and dark-blue balls are O, Ca, and Co respectively.

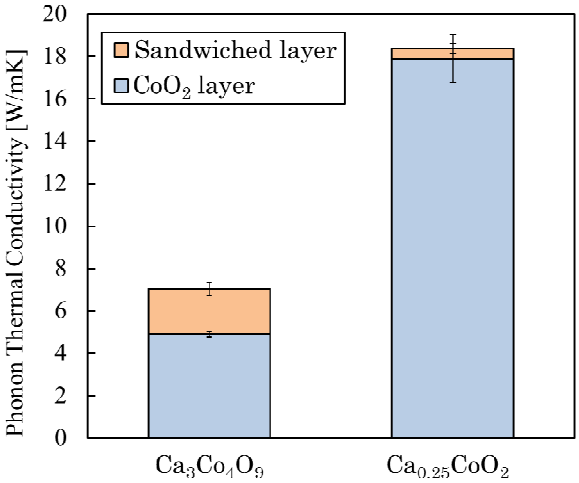


FIG. 2. In plane phonon thermal conductivity of two layered calcium cobaltites at 300 K

TABLE 1. In plane phonon thermal conductivity [W/mK] of Sr-doped $Ca_3Co_4O_9$ at 300 K

Sr doping [%]	0	15	100
Total	7.03	5.35	9.86
CoO_2 layer	4.90	4.13	6.04
Ca_2CoO_3 layer	2.13	1.23	3.82