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Numerical Analyses on Realization of Low Thermal Conductivity without Degrading High Electronic Conductivity in $Na_{0.5}CoO_2$

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Layered cobalt oxide thermoelectric (TE) materials have been paid increasing attention, since they exhibit a high figure of merit and cost less than conventional Bi-Te. These materials composed of Co-O layers and cation layers, stacking alternatively. It is known that this individual atomic structure enables to generate high Seebeck coefficient and high in-plane electronic conductivity, which are required for a high figure of merit. That was reported Co-O layers play important rolls for these electronic properties [1-2]. However, knowledge about thermal conductivity, another factor to determine a figure of merit, is still limited, since theories of thermal conduction based on metals or metalloids cannot be directly applied to oxides having more complicated crystal structures. In order to open up a new era of these TE materials, detailed mechanisms of thermal conduction need to be clarified. In TE materials, low phonon thermal conductivity is required to keep temperature difference. Since high electronic conduction is required, which inevitably accompanies high electronic thermal conductivity, low phonon thermal conductivity is important for high performance of TE materials. Therefore, we have aimed at revealing mechanisms governing phonon thermal conduction in layered cobalt oxides. In order to do so, computational analysis by molecular dynamics has been carried out. Phonon thermal conductivity can be obtained by perturbed molecular dynamics calculation [3], which also enables to calculate partial phonon thermal conductivity, contribution of each constituent element to overall phonon thermal conductivity.

Na_xCoO_2 is one of the layered cobalt oxide TE materials, which has the simplest crystal structure, composed of Na layers stacked between Co-O layers. It is known that $Na_{0.5}CoO_2$ that contains Na vacancies as many as Na atoms, exhibits a high figure of merit at high temperatures [4]. We analyzed atomic vibration of $Na_{0.5}CoO_2$ with molecular dynamics using pairwise potentials determined by first principle calculations [5]. From this calculation, we obtained mean square displacements (MSD) of each constituent element. Figure 1 shows the MSDs of Co and O in $Na_{0.5}CoO_2$ at 300 K. In this figure, two lines of Co and O are quite similar as evidenced by correlation coefficient of over 0.99 between them although that between Na and O, of which MSD is not shown in Fig. 1, was about 0.24. This result indicates that Co and O vibrate in a coupled manner. In addition, in-plane phonon thermal conductivity of $NaCoO_2$ in comparison with $Na_{0.5}CoO_2$ was calculated and it is confirmed that introduction of Na vacancies reduce phonon thermal conductivity compared with that of $NaCoO_2$ that has no Na vacancy. Assuming the kinetic theory of gas holds also for these solid compounds, the phonon thermal conductivity, κ_{phonon}, can be described as the product of heat capacity, C, phonon group velocity, v, and phonon mean free path, l:

$$\kappa_{phonon} = 1/3 \cdot Cvl \qquad (1)$$

This equation enables to clarify which of the three factors is responsible for the decrease in phonon thermal conductivity. C and v were obtained as the gradient of internal energy

of the system with respect to temperature and as the average of gradients of the phonon dispersion curves of three acoustic modes at Γ point, respectively. Table 1 compares *C*, *v*, and *l* of $Na_{0.5}CoO_2$ and $NaCoO_2$ at 300 K. Decreases in *C* and *v* of $Na_{0.5}CoO_2$ from those of $NaCoO_2$ were not as large as the decrease in phonon thermal conductivity, which indicates that remaining phonon mean free path is responsible for the decrease in phonon thermal conductivity due to introduction of Na vacancies [6]. From analysis of partial phonon thermal conductivity (Fig 2), the phonon thermal conductivity is dominated by contributions of Co and O, while contribution of Na is modest in both $Na_{0.5}CoO_2$ and $NaCoO_2$ [7]. This figure also shows introduction of Na vacancies not only decrease the contribution of Na but also significantly alter the contribution of Co and O. These results suggest that introduction of Na vacancies drastically reduced the phonon mean free path in Co-O layers without affecting relative structure of Co-O layers and this would enable $Na_{0.5}CoO_2$ to attain low thermal conductivity together with high electric conductivity.

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References

[1] T. Kawata et al., *Phys. Rev. B*, **60**, (1999) 10584-10587.
[2] W. Koshibae et al, *Phys. Rev. B*, **62**, (2000) 6869-6872.
[3] M. Yoshiya et al, *Mol. Simulat.*, **30**, (2004) 953-961.
[4] I. Terasaki, *Phys. Rev. B*, **56**, (1997) R12685-R12687.
[5] M. Tada et al, *Trans. Mater. Res. Soc. Jpn.*, (2010) *in press*.
[6] M. Tada et al, *J. Electron. Mater.*, (2010) *in press*.
[7] M. Tada et al, *AMTC Lett.*, **1**, (2008) 166-167

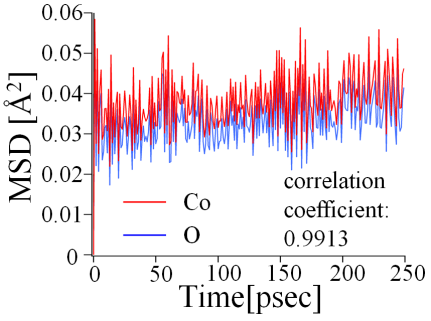

FIG. 1. MSD of Co and O in $Na_{0.5}CoO_2$ at 300 K

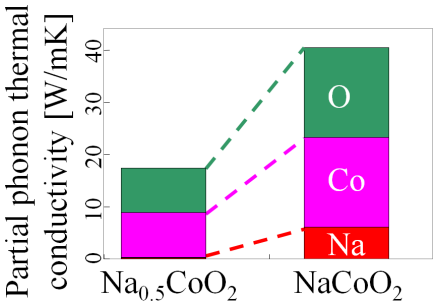

FIG. 2. Partial phonon thermal conductivity of Na_xCoO_2 (x=0.5, 1) at 300 K

TABLE 1. Heat capacity, *C*, phonon group velocity, *v*, and phonon thermal conductivity, κ_{phonon} of $NaCoO_2$ and $Na_{0.5}CoO_2$ at 300 K with ratio of decrease of $Na_{0.5}CoO_2$ from $NaCoO_2$

at 300K	*C* [J/(K mol)]	*v* [km/s]	*l* [Å]	κ_{phonon} [J/m K]
$NaCoO_2$	25.0	1.04	45.1	41.6
$Na_{0.5}CoO_2$	24.8	0.946	28.3	20.9
decrease ratio	0.80%	9.18%	37.2%	49.8%