

Effects of Na vacancies on phonon thermal conductivity of Na_xCoO_2 by perturbed molecular dynamics

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Emergence of layered oxide thermoelectric materials, including Na_xCoO_2 [1] and Ca-Co-O [2], opens up a new era of thermoelectric materials which convert temperature difference to electric potential difference. They have high Seebeck coefficients and high electronic conductivity as well as modest values of thermal conductivity, which yield higher value figure of merit than it has ever been expected for oxides. As for electronic parts of their properties, it has been extensively studied thus far and those studies have revealed that strongly-correlated 3d electrons and high concentration of carrier are responsible for high figure of merit of these series of materials. Besides, detailed mechanism of high Seebeck coefficient has been elucidated[3] from theoretical points of view. In contrast, details of the thermal conduction mechanism is still unclear since it is difficult in experiment to obtain enough large single crystals with controlled chemistry to analyze directional thermal conduction, thereby confirms the above idea, which impedes further development of the materials toward higher figure of merit. But it has been believed that low thermal conductivity of Na_xCoO_2 is realized by vacancies in Na layers. In the present study, we have carried out perturbed molecular dynamics simulation, using pairwise potential parameters derived from first principles calculations, to predict thermal conductivity in an idealized condition in which chemistry and crystal structure are well determined, as well as to analyze underlying physics that determine phonon thermal conductivity. Especially, we focus on effects of sodium vacancies on the phonon thermal conductivity using several virtual models in which fictitious atoms eliminate a scattering factor to determine scatterer responsible for the decrease in thermal conductivity as observed in experiment.

First, we prepared models of NaCoO_2 and $\text{Na}_{0.5}\text{CoO}_2$ which include sodium vacancies as the ratio of 50% determined by first principle calculation, in order to understand dependence of atomic motions on sodium vacancies by molecular dynamics. It requires inter-atomic potentials in prior to simulation. However, no potential parameter suitable for these materials has been reported. So, to obtain the potential parameter sets by fitting, we have carried out first principles calculations to determine fitting targets, including lattice constants, atomic coordinates, and elastic constants. Since ionic bond can be expressed sufficiently by interaction between two atoms in general, we employed Buckingham form of the two-body pair-wise potential function in this study and determine the parameter set for these materials. The potential parameter set was determined so that lattice constants and elastic constants calculated using the potentials reproduce those obtained by the first principles calculation. In this fitting procedure, we also try to reproduce Na_2O and Co_3O_4 as well as Na_xCoO_2 . In other words, these potentials were not specialized for Na_xCoO_2 . This fitting with these binary oxides makes the potential parameter set more reliable in terms of physics. Crystal structures obtained by first principles are in good agreement with those calculated by pair-wise potentials, with errors below 1.3 %. Values calculated using pair-wise potential are also in good agreement with experiment, with errors below 2.1 %. And agreements in elastic constants are not as good as those in lattice constants, with errors about 30%. However, an error in elastic constants results in an error in amplitude of atomic vibration in square root manner: An error by 30% results in only 1.14 times larger amplitude of atomic vibration, so these agreements are satisfactory.

Using these pair-wise potential set, we have carried out perturbed molecular dynamics using Newton's equation of motion with a perturbation term:

$$\dot{\mathbf{r}}_i = \mathbf{p}_i / m_i \quad \text{and} \quad (1)$$

$$\dot{\mathbf{p}}_i = \mathbf{F}_i + \mathbf{D}_i \cdot \mathbf{F}_{ext} \quad (2)$$

where $\dot{\mathbf{r}}_i$ and $\dot{\mathbf{p}}_i$ are time derivatives of atomic position and momentum vectors, and m_i is mass of atom i . \mathbf{F}_i is a sum of forces exerted on atom i and \mathbf{D}_i is a second rank tensor and is determined from

microscopic heat flux vector, \mathbf{J} , so that they satisfy the relationship

$$\mathbf{J} = \sum_i (\mathbf{p}_i \cdot \mathbf{D}_i / m_i). \quad (3)$$

Although \mathbf{F}_{ext} determines magnitude of perturbation applied to the system, its influence is cancelled out upon calculating thermal conductivity, κ , by

$$\kappa = V / \mathbf{F}_{ext} T \lim_{t \rightarrow \infty} \langle J_x \rangle_t \quad (4)$$

where T is temperature and J_x is heat flux along x -axis. This method enables to calculate phonon thermal conductivity of model[4] as well as partial thermal conductivity, which reveals contribution of each elemental atoms to phonon thermal conductivity.

Figure 1 shows calculated phonon thermal conductivity of NaCoO_2 and $\text{Na}_{0.5}\text{CoO}_2$ along a -axis. In whole range of temperature in the figure, the phonon thermal conductivity of $\text{Na}_{0.5}\text{CoO}_2$ is lower than that of NaCoO_2 : The presence of Na vacancies in Na_xCoO_2 significantly reduces the phonon thermal conductivity. Figure 2 shows calculated partial phonon thermal conductivity of each model. The phonon thermal conductivity consists mainly of Co and O and contribution of Na is modest in both models. Besides, partial thermal conductivity of Co which is the heaviest element is as much as that of O which is the lightest element. This tendency is also seen in $\text{Na}_{0.5}\text{CoO}_2$ model in which sodium vacancies occupies half of Na sites. From careful observation of atomic motion, it is found that the bond lengths between cobalt and oxygen hardly change as if cobalt and oxygen move together. This suggests that cobalt and oxygen vibrate in a cooperative manner. These results indicate that introduction of Na vacancies drastically decrease the phonon thermal conductivity of cobalt and oxygen without affecting relative states of cooperative vibration between cobalt and oxygen. This property might enable to have low thermal conductivity simultaneously with high electric conductivity.

References

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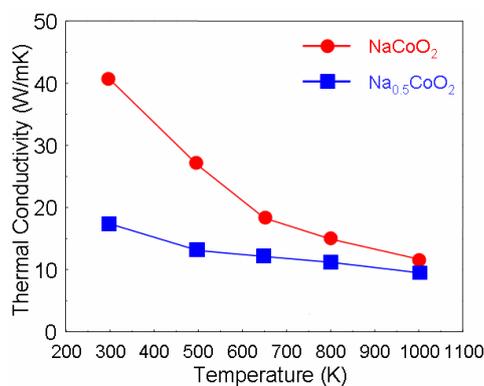


Figure 1. In-plane phonon thermal conductivity

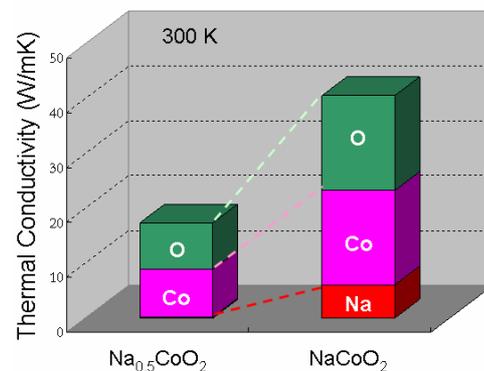


Figure 2. In-plane partial thermal conductivity