Effect of Coulombic Interaction between Layers on Lattice Thermal Conductivity in Na_xCoO_2

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Layered cobalt oxide thermoelectric materials including Na_xCoO_2 exhibit a high figure of merit in metal oxides. Na_xCoO_2 consists of CoO_2 layers and Na layers, stacking alternatively. In order to further develop those materials, it is important to acquire fundamental knowledge as to why the layered oxides have high figure of merit. It is known that these CoO_2 layers enable to generate high Seebeck coefficient and high in-plane electronic conductivity, which are required for a high figure of merit[1)-3)]. However, knowledge about thermal conductivity, another factor of a figure of merit, is still unclear. We have aimed at revealing what governs lattice thermal conduction in the layered cobalt oxides. The lattice thermal conductivity can be obtained by perturbed molecular dynamics calculation[4)]. We have reported that CoO_2 layers in these layered cobalt oxide mainly conduct thermal energy and that phonon scattering in the CoO_2 layers caused by Na vacancies decreases lattice thermal conductivity[5)]. The magnitude of decrease of lattice thermal conductivity can be controlled by distance between Na layer and CoO_2 layer according to comparison among Li_xCoO_2, Na_xCoO_2 and K_xCoO_2[6)]. In this paper, effect of Coulomb interaction difference between Na layer and CoO_2 layer on lattice thermal conductivity is reported: Na_xCoO_2 was compared with Ca_xCoO_2 where Ca^{2+} has similar ion radius to Na^+ and twice as much valence as Na.

An initial crystal structure of $Na_{0.5}CoO_2$ determined with first principle calculation reproduced a reported crystal structure. Distribution of Co^{3+} and Co^{4+} was determined by Co-O distance in the initial crystal structure. In order to prepare a crystal structure of $Na_{0.25}CoO_2$, half of Na which is right above Co site in $Na_{0.5}CoO_2$ was eliminated. Distribution of valences of Co was determined so as to minimize inner energy of $Na_{0.5}CoO_2$. Crystal structures of Ca_xCoO_2 were obtained by exchanging Na in Na_xCoO_2 for Ca. Lattice thermal conductivity was obtained by perturbed molecular dynamics calculations. Atomic interactions were described with an empirical pair-wise potential set using Buckingham function.

Out-of-plane lattice constants, thickness of CoO_2 layer, and distance between each CoO_2 layer in $Na_{0.5}CoO_2$ and $Ca_{0.5}CoO_2$ are shown in Table 1. There is not so much difference in lattice constants. However, relation between the thickness and the distance of CoO_2 layer has difference because Ca more strongly attracts O by Coulomb force. Lattice thermal conductivity of Na_xCoO_2 and Ca_xCoO_2 at 300 K is shown in table 2. The thermal conductivity of $Na_{0.25}CoO_2$ is higher than $Na_{0.5}CoO_2$. $Na_{0.25}CoO_2$ has only one crystallographically identical Na site while $Na_{0.5}CoO_2$ has two different sites. Therefore crystal structure of $Na_{0.25}CoO_2$ is more ordered. This indicates that thermal conductivity is affected by Na site ordering.

Ratio of Co^{3+}:Co^{4+} is 1:1 and 1:0 in $Na_{0.5}CoO_2$ and $Ca_{0.5}CoO_2$, respectively. Even if site occupancy x is kept at the same for both Na_xCoO_2 and Ca_xCoO_2, spatial

distribution of Co valences would be different. In order to eliminate the effect of this difference, models in which valence of Co was averaged and distributed evenly was prepared and thermal conductivity was calculated. The calculation is carried out at 250 K to prevent structural change of either model to enable strict comparison. In the result shown in Table 3, lattice thermal conductivity of Ca_xCoO_2 is lower than that of Na_xCoO_2. The lower thermal conductivity of Ca_xCoO_2 is caused by low partial thermal conductivity of CoO_2 layers. The CoO_2 layers consist of CoO_6 octahedra. About distortion of the CoO_6 octahedra, average Co-O distance in CoO_6 and its deviation is shown in Table 4, which shows that CoO_6 octahedra in Ca_xCoO_2 have larger deviation. This indicates that strong Coulomb attractive force between Ca and O distorts CoO_6 octahedra and this distortion decrease lattice thermal conductivity of Ca_xCoO_2.

In summary, comparison of lattice thermal conductivity of Na_xCoO_2 and Ca_xCoO_2 indicates that Change in interlayer Coulombic interaction brings about significant change in CoO_6 distortion, and, in turn, thermal conductivity of these layered oxides. Besides, from the comparison of lattice thermal conductivity of $Na_{0.5}CoO_2$ and $Na_{0.25}CoO_2$, lattice thermal conductivity can be affected by site ordering of Na site.

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References: [1] I. Terasaki, *Phys. Rev. B*, **56** (1997) R12685. [2] T. Kawata et al., *Phys. Rev. B*, **60** (1999) 10584. [3] W. Koshibae et al, *Phys. Rev. B*, **62** (2000) 6869. [4] M. Yoshiya et al, *Mol. Simulat.*, **30** (2004) 953. [5] M. Tada et al, *AMTC Lett.*, **2** (2010) 190. [6] M. Tada et al, *J. Electron. Mater.*, **39** (2010) 1439.

Table 1. Thickness of each layer in $Na_{0.5}CoO_2$ and $Ca_{0.5}CoO_2$

	$Na_{0.5}CoO_2$	difference [%] →	$Ca_{0.5}CoO_2$
thickness of CoO_2 layer [Å]	1.94	+3.2	2.00
distance between each CoO_2 layer [Å]	3.64	−7.0	3.39
out-of-plane lattice constant, c [Å]	11.17	−3.5	10.77

Table 2. In plane lattice thermal conductivity [W/mK] at 300 K

	Na_xCoO_2		Ca_xCoO_2	
	$x = 0.5$	$x = 0.25$	$x = 0.5$	$x = 0.25$
Total	19.0	20.0	16.9	18.4
Na layer	0.825	0.109	1.12	0.482
CoO_2 layer	18.2	19.9	15.7	17.9

Table 3. In plane lattice thermal conductivity [W/mK] at 250 K (Co valence evenly distributed)

	Na_xCoO_2		Ca_xCoO_2	
	$x = 0.5$	$x = 0.25$	$x = 0.5$	$x = 0.25$
Total	56.8	36.6	35.7	27.5
Na layer	4.33	0.518	6.75	0.851
CoO_2 layer	52.5	36.1	29.0	26.7

Table 4. Distortion of CoO_6 octahedra

	$Na_{0.5}CoO_2$	$Ca_{0.5}CoO_2$	$Na_{0.25}CoO_2$	$Ca_{0.25}CoO_2$
(a)Co-O distance [Å]	1.80	1.92	1.75	1.80
(b)deviation [Å]	0.0136	0.0343	0.0166	0.0382
(b)/(a) [%]	0.755	1.79	0.946	2.12