Restoration of long range order of Na ions in Na$_x$CoO$_2$ at high temperatures by sodium site doping

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We have systematically investigated the Na$_x$CoO$_2$ system doped with Cu, Y, Sn, W, Au and Bi for $x = 0.5, 0.75$ and $1.00$ using density functional theory. Sn, W, and Bi always substitute a Co while Au always substitutes a Na regardless of Na concentration. However, for Cu and Y, the substitution site depends on Na concentration. When compared to the available experimental data, we find that thermoelectric performance is enhanced when the dopants substitute a Na site. In this case, surprisingly, resistivity decreases despite the reduced hole concentration caused by carrier recombination. We propose improved carrier mobility to be the cause of observed reduced resistivity.

Keywords: Density functional theory, Sodium cobaltate, Doping, Thermoelectric effect

I. INTRODUCTION

Layered sodium cobaltate (Na$_x$CoO$_2$) is a fascinating material that has exotic magnetic, thermoelectric and superconducting properties. For $0.5 < x < 1$, polycrystalline Na$_x$CoO$_2$ has a comparatively high figure of merit ($ZT$) of $0.8$ at temperature ($T$) range of $800 - 1000$ K. This $ZT$ is unusually high for an oxide. As shown in Fig. 1, Na$_x$CoO$_2$ lattice consists of alternating Na layers and edge-sharing CoO$_6$ octahedral layers. In Na deficient systems ($x < 1$), the Na ions adopt various configurations within their plane lowering crystal’s symmetry. Furthermore, due to high Na diffusivity (schematically indicated by grey arrows in Fig. 1), the Na layer is highly disordered by randomly distributed vacant sites in temperatures above ambient thus creating a medium that disturbs the propagation of phonon excitations. This irregular and dynamic positioning of the Na ions, therefore, considerably reduces the lattice thermal conductivity ($\kappa_L$) to $0.01$ W cm$^{-1}$K$^{-1}$ at $T = 1000$ K. This is in contrast to most oxides in which the dominance of covalent bonding causes relatively high $\kappa_L$; for instance, ZnO has a $\kappa_L$ value of $1.25$ W cm$^{-1}$K$^{-1}$ at $T = 1000$ K. However, the irregular pattern of Na ions comes with the disadvantage of low carrier mobility which is in the range of $0.8$ cm$^2$V$^{-1}$s$^{-1}$ for Na$_x$CoO$_2$ at room temperature (compared to $205$ cm$^2$V$^{-1}$s$^{-1}$ of ZnO at the same temperature range). The lower charge carrier mobility is nonetheless partly compensated by high carrier concentrations ($n$) which is in order of $10^{21}$ to $10^{22}$ cm$^{-3}$ for Na$_{0.5}$CoO$_2$. We should notice that this level of carrier concentration is also unusually high for a good thermoelectric semiconductor which has been demonstrated to be $10^{19}$ cm$^{-3}$.

In order to further improve the thermoelectric performance of Na$_x$CoO$_2$, doping has extensively been used to increase the $ZT$ of Na$_x$CoO$_2$. Nonetheless, the choice of dopants has usually been restricted by the solubility limits and mechanical and chemical restrictions imposed by the fabrication techniques. As a result, the experimental advancement in the doped Na$_x$CoO$_2$ has been mainly guided by the practical consideration rather comprehensive and strategic attempt to improve the factors influencing the $ZT$. Consequently, not only the initial ambition of a figure of merit comfortably greater than one was not realized, but also many theoretically interesting questions remained unanswered too. One of these questions that we try to address here is how carrier mobility is affected by the dopants and how this is reflected on the thermoelectric performance. Fig. 2 shows the Seebeck coefficient ($a$) and electrical resistivity ($b$) of Na$_x$CoO$_2$ doped with a wide variety of dopants as reported in the literature for $T = 800$ K. After inspection, we notice that (i) the highest Seebeck coefficient is obtained for late transition elements dopants like Cu and Zn for which the Seebeck coefficient exceeds $180$ $\mu$VK$^{-1}$; (ii) the highest Seebeck coefficient is achieved when $x = 0.5$ as higher Na concentrations consistently result in lower Seebeck coefficient; (iii) the lowest resistivity is achieved for dopant concentrations of $2.5$% or lower. Higher dopant concentrations result in the higher resistivity ($\rho$), sometimes by few orders of magnitude. To interpret these experimental results, we conducted a comprehensive theoretical study of the Na$_x$CoO$_2$:M system in which $x = 0.5, 0.75$ and $1.00$ while M = Cu, Y, Sn, W, Au and Bi, representing different element groups.

II. COMPUTATIONAL DETAILS

We performed $ab$ initio spin-polarized density functional calculations using Accelrys’s DMol$^3$ package. Self-consistent energy calculations were performed with double-numeric plus polarization basis and generalized gradient approximation based on Perdew-Wang formalism for the exchange-correlation functional. Real-space global cut-off radii were set for all elements at 6.00 Å, and Brillouin zone sampling was carried out by choosing a $2 \times 4 \times 2$ $k$-point set within Monkhorst-Pack

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scheme with a grid spacing of $\sim 0.05\ \text{Å}^{-1}$ between $k$ points. The geometry optimization convergence thresholds for energy, Cartesian components of internal forces acting on the ions, and displacement were set to be $10^{-5}\text{eV/atom}$, $0.01\text{eV/Å}$, and $0.005\text{Å}$. A $4a \times 2a \times 1c$ supercell of Na$_{16}$Co$_{16}$O$_{32}$ constructed for studying the doped systems. To vary sodium concentration, four or eight sodium ions were removed from the original supercell to create Na$_{12}$Co$_{16}$Co$_{32}$ and Na$_{8}$Co$_{16}$O$_{32}$ supercells for which $x = 0.75$ and 0.50 respectively. The overall crystal structure of Na$_x$CoO$_2$ and the ordering of Na ions critically depends on the Na concentration and has been extensively investigated both experimentally and theoretically.$^{22-24}$ In this work, the Na patterns in the supercell for different values of $x$ were adopted after our previous work.$^{25}$ Since we only considered dopants that replaced cations, dopants’ formation energy ($E^f$) was calculated for four possible geometric configurations. In the first configuration, M substituted Na ion at Na1 site creating a M$_{Na1}$ configuration. In the second configuration, M substituted a Na ion at Na2 site creating a M$_{Na2}$ configuration. Na1 shares basal with Co and occupies the Wyckoff site $b$ while Na2 site shares the basal coordinates with O and occupies the Wyckoff site $d$ of the $P6_3/mmc$ NaCoO$_2$ primitive cell as demonstrated in Fig. 1. In the third configuration, M occupied an interstitial site in Na layer creating a M$_{Int}$ configuration. Few distinct positions for the M$_{Int}$ configuration were considered. We found that the interstitial dopants are more stable when located on a vacant Na2 (or Wyckoff $d$) position. Finally, the fourth configuration is constructed by M substituting a Co ion creating a M$_{Co}$ configuration. One special case was the M$_{Na1}$ for $x = 1$; since in NaCoO$_2$, all Na ions were located in Na2 location, no stable local minimum for M$_{Na1}$ was found; all M$_{Na1}$ dopants instead relaxed to Na2 location. The formation energy ($E^f$) was calculated using the standard procedure as described by the following equation:

$$E^f = E^t (Na_xCoO_2:M) + \mu_{\alpha} - E^t (Na_xCoO_2) - \mu_M \quad (1)$$

Here, $E^t (Na_xCoO_2:M)$ is the total energy of the Na$_x$CoO$_2$ supercell containing the dopant M and $E^t (Na_xCoO_2)$ is the total energy of the pristine Na$_x$CoO$_2$ supercell. $\mu_{\alpha}$ and $\mu_M$ are the chemical potentials of the removed and added elements respectively. The chemical potentials were calculated from the total energies of their most stable oxides representing an oxygen-rich condition except for Au were the chemical potential was calculated from the total energy of Au’s metallic form. The formation energy of the dopants in Na$_x$CoO$_2$ is presented in Fig. 2 (a)-(f).
III. RESULTS AND DISCUSSION

In the case of Cu doping, for \( x = 0.5 \), \( \text{Cu}_{\text{Int}} \) had the lowest formation energy of 1.45 eV. However, for \( x = 0.75 \) and 1.00, the most stable configuration was \( \text{Cu}_{\text{Co}} \) with formation energy of 2.49 eV and 1.29 eV respectively. In the \( \text{Na}_x\text{CoO}_2\cdot\text{Y} \) system, \( Y_{\text{Na}1} \) had the lowest formation energy of 2.59 eV for \( x = 0.5 \). For higher Na concentrations, on the other hand, in a trend similar to the case of Cu doping, the most stable configuration was \( Y_{\text{Co}} \) with formation energy of 3.94 eV for \( x = 0.75 \) and 3.74 eV for \( x = 1.00 \). In the case of Sn doping, \( \text{Sn}_{\text{Co}} \) always had the lowest formation energy for all considered Na concentrations. In this case, \( \text{Sn}_{\text{Co}} \) had an \( E_f \) of \(-1.06\) eV, \(-0.94\) eV and \(-0.53\) eV for \( x = 0.5, 0.75 \) and 1.00 respectively. For the \( \text{Na}_x\text{CoO}_2\cdot\text{W} \) system, \( \text{W}_{\text{Co}} \) was the most stable configuration for all values of \( x \) having an \( E_f \) of \( 3.68 \) eV, \( 4.40 \) eV and \( 4.86 \) eV for \( x = 0.50, 0.75 \) and 1.00 respectively. In the \( \text{Na}_x\text{CoO}_2\cdot\text{Au} \) system, \( \text{Au}_{\text{Int}} \) was the most stable structure for \( x = 0.5 \) with an \( E_f \) of 0.87 eV. For \( x = 0.75 \) the most stable configuration was \( \text{Au}_{\text{Na}1} \) with an \( E_f \) of \( 1.88 \) eV and for \( x = 1.00 \), \( \text{Au}_{\text{Na}2} \) was the most stable configuration with an \( E_f \) of 2.01 eV. For the \( \text{Na}_x\text{CoO}_2\cdot\text{Bi} \) system, \( \text{Bi}_{\text{Co}} \) was the most stable configuration for all considered Na concentrations having an \( E_f \) of \( 2.16 \) eV, \( 2.89 \) eV and \( 3.89 \) eV for \( x = 0.5, 0.75 \) and 1.00 respectively.

We can classify these dopants in three different categories; the ones that always substitute a Co regardless of Na concentration like Bi, W and Sn; the one that is always located in the Na layer namely Au regardless of Na concentration; and the ones for which the most stable configuration depends on Na concentration. The latter ones, Cu and Y, are located in the Na layer for lower Na concentration, i.e. \( x = 0.5 \), but they become more stable when substituting Co at higher Na concentrations. By comparing the DFT results with the experiments, we find that Cu and Au dopants that best improve the thermoelectric properties reside in the Na layer for \( x = 0.5 \). Furthermore, our previous investigation has also shown that the rare earth element Eu that improves the thermoelectric performance also resides on the Na layer.

A dopant with an oxidation state more than 1+ that replaces a Na ion reduces the carrier concentration through electron-hole recombination by compensating for the Na vacancy in the \( \text{Na}_x\text{CoO}_2 \) system (stoichiometric \( \text{NaCoO}_2 \) is a band insulator). This is also true for any cationic dopant that is placed in Na layer interstitially. As a consequence, one anticipates an increase in the electrical resistivity by doping such an element. The experimental data, however, obviously indicate the opposite. In one instance, where comprehensive experimental data were available, the resistivity of undoped \( \text{Na}_0.75\text{CoO}_2 \) was 83 \( \mu\Omega \cdot \text{m} \) at \( T = 800 \) K while introducing 2.5%, 5%, 7.5% and 10% of Cu reduced \( \rho \) to 76 \( \mu\Omega \cdot \text{m} \), 54 \( \mu\Omega \cdot \text{m} \), 51 \( \mu\Omega \cdot \text{m} \) and 50 \( \mu\Omega \cdot \text{m} \) respectively, as represented by black circles in Fig. 4. A similar effect was also observed for Ag doped \( \text{Na}_0.75\text{CoO}_2 \) which is directly veri-
FIG. 4. The black circles represent the resistivity measurement of Na$_{0.5}$CoO$_2$:Cu adopted from the work of Park et al.\cite{14} The hole density was calculated assuming that Cu is incorporated in the Ns layer interstitially. The mobility was calculated by assuming that only holes contribute to conduction. The mobility data were fitted with a growth function, and it was found that Cu$_{\text{Int}}$ raises the mobility to the values at ambient as measured by Brinks et al.\cite{7}

fied for other dopants by experiments where the dopants are incorporated in the Na layer. For example, Raman spectroscopy measurement detected the peaks of Na ordering at room temperatures in Mg$_{\text{Na}}$ doped Na$_{0.8}$CoO$_2$ system. These peaks were absent in the undoped samples at the same temperature.\cite{29} Furthermore, neutron diffraction experiments have shown that Ca doping in Na layer creates a Na superlattice ordered over long range at temperatures as high as 490 K.\cite{30} This in contrast to the behaviour of Na ions in undoped Na$_{0.5}$CoO$_2$ in which the superstructures of tri-vacancy in Na layer vanishes at temperatures higher than 200 K.\cite{31} To further examine this idea, we calculated the carrier mobility for different Cu concentration in Na$_{0.5}$CoO$_2$:Cu at 800 K.\cite{14} By examining the Mulliken charge population of Cu$_{\text{Int}}$ (the most stable configuration of Cu in Na$_{0.5}$CoO$_2$ according to Fig. 3(a)), we found that Cu’s 3$d$ orbitals were occupied by $\sim$ 9.75 electrons implying that Cu had an oxidation state of $\sim$ 1+. Then, accordingly, we adjusted the number of free carrier per unit cell and calculated the carrier concentration ($n$) using the experimental lattice parameters of Na$_{0.5}$CoO$_2$.\cite{32} We further assumed that conductivity is mainly due to the hole carriers and neglect the Na ionic contribution to the conductivity. This assumption is justified by the fact that the ionic conductivity in Na$_{x}$CoO$_2$ is in order of $\sim$ 6 mS/cm\cite{33} (equivalent of a resistivity of $\sim$ 1.67 $\Omega \cdot$m) which is $\sim$ 5 orders of magnitude smaller than the electronic conductivity. Finally, we used the resistivity-mobility relationship $\rho = 1/e\mu n$ to obtain the mobility presented by blue squares in Fig. 4. We see that despite decreasing hole concentration, carrier mobility increases with rising Cu concentration approaching the values of pristine Na$_{x}$CoO$_2$ at ambient.\cite{7} Hence, we can see the direct correlation between the Cu dopant concentration and increased mobility. This interesting phenomenon nonetheless needs to be further investigated by direct experimental probes as it is important not only to the thermoelectric applications but to the rechargeable Na ion batteries.\cite{34}

IV. CONCLUSIONS

In conclusion, guided by experimental results, we performed DFT calculation for Na$_{x}$CoO$_2$ system doped with Cu, Y, Sn, W, Au and Bi. We found that the best thermoelectric performance is achieved when the dopant is located in the Na layer within the Na$_{x}$CoO$_2$ structure. Although these dopants reduce the hole concentration, they have a greater impact increasing carrier mobility, therefore, improving electrical conductivity which is an important contributing factor toward $ZT$. However, the effect of this category of dopants on thermal conductivity should be experimentally investigated to find the extent of the trade-off between improving carrier mobility and increasing lattice thermal conductivity.

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U. Ozgur, X. Gu, S. Chevtchenko, J. Spradlin, S. J. Cho, H. Morkoc, F. H. Pollak, H. O. Everitt, B. Nemeth, and J. E. Nause, J. Electron. Mater. 35, 550 (2006).

P. Brinks, G. Rijnders, and M. Huijben, Appl. Phys. Lett. 105, 193902 (2014).

D. C. Look, D. C. Reynolds, J. R. Sizelove, R. L. Jones, C. W. Litton, G. Cantwell, and W. C. Harsch, Solid State Commun. 105, 399 (1998).

I. Terasaki, I. Tsukada, and Y. Iguchi, Phys. Rev. B 65, 195106 (2002).

S. W. Li, R. Funahashi, I. Matsubara, and S. Sodeoka, Mater. Res. Bull. 35, 2371 (2000).

T. Nagira, M. Ito, and S. Hara, Mater. Trans. 45, 1339 (2004).

T. Seetawan, V. Amornkitbamrung, T. Burinprakhon, S. Maensiri, K. Kurosaki, H. Muta, M. Uno, and S. Yamana, J. Alloy. Compd. 407, 314 (2006).

M. Ito, T. Nagira, and S. Hara, J. Alloy. Compd. 408, 1217 (2006).

K. Park, K. U. Jang, H. C. Kwon, J. G. Kim, and W. S. Cho, J. Alloy. Compd. 419, 213 (2006).

M. Ito and D. Furumoto, J. Alloy. Compd. 450, 494 (2008).

K. Park and J. H. Lee, Mater. Lett. 62, 2366 (2008).

L. Wang, M. Wang, and D. Zhao, J. Alloy. Compd. 471, 519 (2009).

P. H. Tsai, T. S. Zhang, R. Donelson, T. T. Tan, and S. Li, J. Alloy. Compd. 509, 5183 (2011).

B. Delley, J. Chem. Phys. 92, 508 (1990).

B. Delley, J. Chem. Phys. 113, 7756 (2000).

J. Perdew and Y. Wang, Phys. Rev. B 45, 13244 (1992).

H. W. Zandbergen, M. Foo, Q. Xu, V. Kumar, and R. J. Cava, Phys. Rev. B 70, 024101 (2004).

P. Zhang, R. B. Capaz, M. L. Cohen, and S. G. Louie, Phys. Rev. B 71, 153102 (2005).

Y. S. Meng, A. Van der Ven, M. K. Y. Chan, and G. Ceder, Phys. Rev. B 72, 172103 (2005).

M. H. N. Assadi and H. Katayama-Yoshida, Funct. Mater. Lett. 08, 1540016 (2015).

M. H. N. Assadi, S. Li, and A. B. Yu, RSC Adv. 3, 1442 (2013).

G. Lang, J. Bobroff, H. Alloul, P. Mendels, N. Blanchard, and G. Collin, Phys. Rev. B 72, 094404 (2005).

F. Battogg, A. Sacchetti, H. R. Ott, K. Mattenberger, and B. Batlogg, Phys. Rev. Lett. 102, 056401 (2009).

P. H. Tsai, M. H. N. Assadi, T. Zhang, C. Ulrich, T. T. Tan, R. Donelson, and S. Li, J. Phys. Chem. C 116, 4324 (2012).

D. G. Porter, M. Roger, M. J. Gutmann, S. Uthayakumar, D. Prabhakaran, A. T. Boothroyd, M. S. Pandiyan, and J. P. Goff, Phys. Rev. B 90, 054101 (2014).

D. J. Voneshen, K. Refson, E. Borissenko, M. Krisch, A. Bosak, A. Piovano, E. Cemal, M. Enderle, M. J. Gutmann, M. Hoesch, M. Roger, L. Gannon, A. T. Boothroyd, S. Uthayakumar, D. G. Porter, and J. P. Goff, Nat. Mater. 12, 1027 (2013).

D. P. Chen, H. C. Chen, A. Maljuk, A. Kulakov, H. Zhang, P. Lemmens, and C. T. Lin, Phys. Rev. B 70, 024506 (2004).

Y. Mo, S. P. Ong, and G. Ceder, Chem. Mater. 26, 5208 (2014).

S. C. Han, H. Lim, J. Jeong, D. Ahn, W. B. Park, K.-S. Sohn, and M. Pyo, J. Power Sources 277, 9 (2015).