Na site doping a pathway for enhanced thermoelectric performance in Na$_{1-x}$CoO$_2$; the case of Gd and Yb dopants

M Hussein N Assadi

School of Materials Science and Engineering, UNSW Australia, Sydney, NSW 2052, Australia

E-mail: h.assadi.2008@ieee.org

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Abstract
Doping is considered to be the main method for improving the thermoelectric performance of layered sodium cobaltate (Na$_{1-x}$CoO$_2$). However, in the vast majority of past reports, the equilibrium location of the dopant in the Na$_{1-x}$CoO$_2$ complex layered lattice has not been confidently identified. Consequently, a universal strategy for choosing a suitable dopant for enhancing Na$_{1-x}$CoO$_2$’s figure of merit is yet to be established. Here, by examining the formation energy of Gd and Yb dopants in Na$_{0.75}$CoO$_2$ and Na$_{0.50}$CoO$_2$, we demonstrate that in an oxygen poor environment, Gd and Yb dopants reside in the Na layer while in an oxygen rich environment these dopants replace a Co in CoO$_2$ layer. When at Na layer, Gd and Yb dopants reduce the carrier concentration via electron–hole recombination, simultaneously increasing the Seebeck coefficient (S) and reducing electric conductivity (σ). Na site doping, however, improves the thermoelectric power factor (PF), only in Na$_{0.50}$CoO$_2$. When replacing a Co, these dopants reduce S and PF. The results demonstrate how thermoelectric performance critically depends on the synthesis environment that must be fine-tuned for achieving any thermoelectric enhancement.

Keywords:doping, sodium cobaltate, density functional theory, thermoelectric effect

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(Some figures may appear in colour only in the online journal)
limits of the applied synthesis method [33]. An overlooked issue, nonetheless, is that cationic dopants can be principally substituted for either Na or Co ions. Identifying the exact location of the cationic dopant in Na$_{1-x}$CoO$_2$’s lattice under a specific condition requires characterisations sensitive to the local chemical environments such as x-ray absorption spectroscopy and neutron diffraction which are most often absent from the existing reports so far. Consequently, despite the large volume of research on doped Na$_{1-x}$CoO$_2$, the experimental advancement in the doped Na$_{1-x}$CoO$_2$ has been mainly guided by the approximate guesswork rather comprehensive and strategic insight of how dopants influence the $ZT$ through structure-property relationship. As a result, not only the initial ambition of achieving a $ZT$ comfortably greater than one has not been realised yet but also many theoretically interesting questions have remained unanswered.

In this work, therefore, we examine the energetics and the electronic structure of Gd and Yb doped Na$_{1-x}$CoO$_2$ for $x = 0.25$ and 0.5. Based on the formation energy calculations, we demonstrate that the location of Yb and Gd dopants in Na$_{1-x}$CoO$_2$ critically depends on the synthesis environment, i.e. these dopants reside in different lattice sites depending on the O partial pressure during the synthesis. The insight obtained here complements our previous work that demonstrated that the location of dopants such as Cu and Au also depends on the Na content of Na$_{1-x}$CoO$_2$ [34]. One of the main conclusions that we draw in this work is that the location of cationic dopants in Na$_{1-x}$CoO$_2$ needs to be investigated critically and the simplistic assumption based on matching ionic radii in determining dopant location can be misleading at times.

**Computational settings**

Total energy density functional calculations were performed using the plane-wave and on-the-fly generated ultra-soft pseudopotential [35] approach, as implemented in CASTEP [36–38]. Ceperley and Alder’s local density approximation was used for the exchange-correlation term in the Hamiltonian [39]. Energy cut-off was set to 517 eV, and the $k$-point mesh was set to generate a $k$ point separation of 0.05 Å$^{-1}$ for oxides and 0.01 Å$^{-1}$ for metals. The density-mixing scheme was applied for electronic minimisation during which the spin
of all atoms was initiated based on formal values and then allowed to relax. The scalar relativistic treatment based on Koelling–Harmon approximation of Dirac’s equation was also applied [40]. LDA+U correction based on a simplified and rotationally invariant approach was applied to Co 3d and Gd/Yb 4f electrons [41]. The default U values of 2.5 eV for Co and 6.0 eV for rare earth dopants were selected for which a full justification is provided in figure S1 of the supplementary information (stacks.iop.org/JPhysCM/23/125502/mmedia). The lattice parameters of a fully optimised primitive unit cell of Na1CoO2 was found to be 2.87 Å for a and 10.90 Å for c reasonably matching the experimental values [42]. The difference was only 0.07% for a and −1.49% for c. Then a 2a × 4a × 1c Na1CoO2 supercell was constructed for studying the doped compounds. Four and then eight out of the sixteen original Na ions were removed according to the previously established patterns [43], shown in figure 1, to create a Na1₂Co₁₀O₃₂ and Na₈Co₁₆O₃₂ supercells for Na₀.₇₅CoO₂ and Na₀.₅₀CoO₂ compounds, respectively. Further details regarding the convergence with respect to the supercell size is provided in table S1 and figure S2 of the supplementary information. The oxidation state of the dopants and the Co ions was estimated from the magnetisation calculated by Mulliken population analysis and examining the partial density of states. One, however, should note that due to partial covalency in Co–O bond, Co ion magnetisation is slightly smaller than what is anticipated from Hund’s rule [44]. The accuracy of Mulliken population analysis was cross-examined with Hirshfeld charge analysis for with the results are provided in table S2. It was found that Mulliken population analysis provides a robust description of charge localisation in doped Na₁₋ₓCoO₂ compounds.

Results and discussion

Dopants’ formation energy (E₇) was calculated for four possible replacement configurations. In the first configuration, the dopant M replaced a Co ion creating an MCo₈ configuration. In the second instant, M occupied an interstitial site in the Na layer, creating a Mn₈ configuration. Third, dopant M replaced a Na ion at Na1 site, creating an Mn₁₁₈ configuration. As demonstrated in figure 1, Na1 site shares the basal coordinates with Co while Na2 shares the basal coordinates with O. The formation energy (E₇) was calculated using the standard procedure as described by the following equation [45]:

\[ E₇ = E'(Na₁₋ₓCo₂:M) + \mu_α - E'(Na₁₋ₓCo₂) - \mu_M. \]  

(1)

Here, E'(Na₁₋ₓCo₂:M) is the total energy of the Na₁₋ₓCo₂ supercell containing the dopant M, and E'(Na₁₋ₓCo₂) is the total energy of the undoped Na₁₋ₓCo₂ supercell. \( \mu_α \) and \( \mu_M \) are the chemical potentials of the removed and added elements, respectively. The chemical potentials depend on the synthesis environment [46]. To investigate the thermodynamics of dopant solubility in Na₁₋ₓCo₂, we first determined the accessible chemical potentials for Na, Co, O, and the dopants Gd and Yb. By varying the chemical potentials (\( \mu \)) by a permissible value of \( \Delta \mu = \mu^{(i)} + \Delta \mu \), we can simulate the effect of varying the oxygen partial pressures and the abundance of constituting elements on the dopants’ formation energy and their location in the host lattice. We, therefore, can determine the optimum conditions for Gd and Yb doping that may enhance the thermoelectric performance. The first constraint on the chemical potentials is set by the enthalpy of the Na₁₋ₓCo₂:

\[ (1 - x) \Delta \mu_{Na} + \Delta \mu_{Co} + 2\Delta \mu_{O} = \Delta H^f \ (Na₁₋ₓCo₂). \]  

(2)

in which \( \Delta H^f (Na₁₋ₓCo₂) \) is the DFT formation enthalpy of Na₁₋ₓCo₂. Furthermore, to avoid precipitation into solid elemental Co, Na, and the release of gaseous O₂, we also require:

\[ \mu_{Na}, \mu_{Co}, \mu_{O} < 0. \]  

(3)

The chemical potentials are further constrained by the decomposition of Na₁₋ₓCo₂ into competing binary compounds such as Na₂O, CoO₂ and Co₃O₄:

\[ 2\Delta \mu_{Na} + \Delta \mu_{O} = \Delta H^f \ (Na₂O), \quad \Delta \mu_{Co} + 2\Delta \mu_{O} = \Delta H^f \ (CoO₂), \quad 3\Delta \mu_{Co} + 4\Delta \mu_{O} = \Delta H^f \ (Co₃O₄). \]  

(4)

For Gd and Yb, \( \Delta \mu \) was calculated based on:

\[ 2\Delta \mu_{Gd} + 3\Delta \mu_{O} = \Delta H^f \ (Gd₂O₃), \]  

(5)

\[ \Delta \mu_{Yb} + 2\Delta \mu_{O} = \Delta H^f \ (YbO). \]  

(6)

Here Ia₃ Gd₂O₃ and Fm₃m YbO are the most stable Yb and Gd oxides. Finally, the chemical potentials were set equal to the elemental energy of a given metal (\( \mu^{0} \)) plus the corresponding \( \Delta \mu \).

As shown in figure 2, we found that the major limiting phases are Na₂O in Na rich environment and CoO₂ and Co₃O₄ in Co rich environment for both Na₀.₇₅CoO₂ and Na₀.₅₀CoO₂. CoO₂ was not a limiting phase. Furthermore, the available range of the chemical potential was relatively limited by the permissible range of \( \Delta \mu_{Na} \), resulting in a narrow strip that had a wider range for \( \Delta \mu_{Co} \) and \( \Delta \mu_{O} \). Due to the narrow strip of permissible \( \Delta \mu \) values, we only present two extremes when discussing the formation energy. These extremes are marked with A for O poor environment and B for O rich environment in figure 2 (justification is provided in figure S3 and table S3 of the supplementary information).

Figure 3 presents the formation energy of the dopants. Under O poor environment, in Na₀.₅₀CoO₂ and Na₀.₇₅CoO₂, both Gd and Yb dopants reside in the Na layer. In the case of Gd doped Na₀.₇₅CoO₂, GdNa₁ with an \( E^f \) of 5.13 eV was the most stable configuration followed by GdCo₈ with an \( E^f \) of 5.51 eV. In the case of Yd doped Na₀.₇₅CoO₂, YbNa₁ with an \( E^f \) of 14.03 eV was the most stable configuration followed by YbNa₂ with an \( E^f \) of 14.42 eV. In the case of Gd doped Na₀.₅₀CoO₂, the most stable configuration was GdNa₁ with an \( E^f \) of 0.95 eV followed by GdNa₂ with an \( E^f \) of 2.36 eV while in the case of Yb doped Na₀.₅₀CoO₂, the most stable configuration was YbNa₂ with an \( E^f \) of 12.03 eV followed by YbNa₄ with an \( E^f \) of 12.24 eV.
lattice. For Gd doped Na$_{0.75}$CoO$_2$, GdCo with an $E^f$ of 4.95 eV had the lowest energy followed by GdNa$_{1}$ with an $E^f$ of 9.79 eV. For Yb doped Na$_{0.75}$CoO$_2$, YbCo with an $E^f$ of 13.32 eV had the lowest energy followed by YbNa$_{1}$ with an $E^f$ of 14.91 eV. In the case of Gd doped Na$_{0.50}$CoO$_2$, GdCo was the most stable configuration with an $E^f$ of 3.08 eV followed by GdInt with an $E^f$ of 4.31 eV while in the case of Yb doped Na$_{0.50}$CoO$_2$, the most stable YbCo configuration had an $E^f$ of 12.69 eV followed by YbNa$_{2}$ with an $E^f$ of 12.75 eV.

Figure 4 presents the partial density of states (PDOS) of the stable Gd doped configurations in O poor environment, i.e. Na$_{0.75}$CoO$_2$:GdInt and Na$_{0.50}$CoO$_2$:GdInt, and O rich environment, i.e. Na$_{0.75}$CoO$_2$:GdCo and Na$_{0.50}$CoO$_2$:GdCo. In all of these configurations, Gd’s spin-up channel is completely filled while the spin-down channel is empty indicating that Gd adapts an oxidation state of +3 independent from O partial pressure or Na content. Mulliken population analysis also shows a ~7 h/2 magnetisation for Gd in all of these configurations indicating a [Xe] 4f$^7$5d$^0$6s$^0$ electronic configuration, that is Gd$^{3+}$. For GdInt which is stable at O poor environment, the three electrons introduced by the interstitial Gd$^{3+}$ reduce three of the Co$^{3+}$ ions in the Na$_{0.75}$CoO$_2$:GdInt and Na$_{0.50}$CoO$_2$:GdInt to Co$^{3+}$. As a result, Na$_{0.75}$CoO$_2$:GdInt has only one spin bearing Co with a magnetisation of 0.76 h/2 (undoped Na$_{0.75}$CoO$_2$ has a total spin of 3.96 h/2 borne on four out of the 16 Co ions in the supercell commensurate with four low-spin Co$^{4+}$ in tetrahedral coordination i.e. $t_{2g}^5e_{g}^0$), while Na$_{0.50}$CoO$_2$:GdInt has five Co$^{4+}$ ions with a total magnetisation of 4.37 h/2. As marked with arrows in figures 4(a) and (c), the introduction of GdInt has, indeed, reduced the peak height of empty $t_{2g}$ states that indicating a reduction of Co$^{4+}$ concentration. In the case of Na$_{0.75}$CoO$_2$:GdCo, the stable configuration at O rich environment, the total spin borne on Co ions was 3.80 h/2, very close to the value of the undoped compound, indicating that Gd$^{3+}$ has replaced a Co$^{3+}$ ion leaving the four Co$^{4+}$ ions unaltered. The same argument holds for Na$_{0.5}$CoO$_2$:GdCo as the total spin borne on Co ions is 7.2 h/2 indicating eight Co$^{4+}$ in the supercell.

The PDOS of Gd doped compounds has some other noticeable features. For instance, as marked with blue bars in figures 4(b) and (d), the filled spin-up Gd 4f states of GdCo spread over the range of $-6 eV < E_{Fermi} < -4 eV$, while the same states are sharply localised at $-7 eV$ for GdInt for both Gd doped Na$_{0.75}$CoO$_2$ and Na$_{0.50}$CoO$_2$ compounds. The spread of the GdCo 4f states, although not considered full delocalisation, demonstrate the effect of O coordination and its hybridisation with 4f states. Furthermore, the Gd 4f and Co$^{3+}$ 3d ions have parallel spins in all considered compounds in figure 4 except for Na$_{0.50}$CoO$_2$:GdInt for which Gd 4f and Co$^{4+}$ 3d states are of antiparallel spins.

Figure 5 presents the PDOS of Yb doped compounds that are the most stable at O rich and O poor environments, respectively. For compounds that are most stable at O poor environment, that is YbNa$_{1}$ in Na$_{0.75}$CoO$_2$ and YbNa$_{2}$ in Na$_{0.50}$CoO$_2$, Yb 4f states have a narrow empty peak located just above the Fermi level, marked with arrows in figures 5(a) and (c), indicating that Yb dopant had an oxidation state of +3 i.e [Xe] 4f$^{13}$5d$^0$. Considering the remaining spin borne on Co ions which was 1.96 h/2 in Na$_{0.75}$CoO$_2$:YbNa$_{1}$ and 5.12 h/2 in Na$_{0.50}$CoO$_2$:YbNa$_{2}$, we conclude that Yb$^{3+}$ dopants replacing Na$^{1+}$ introduce two electrons into the compounds reducing two Co$^{4+}$. Moreover, Co substituting Yb dopants that are stable in O rich environment also adapted +3 oxidation state as demonstrated by the empty 4f states marked with arrows in figures 5(b) and (d) and the spin borne on Yb ions of 0.95 h/2. In these latter cases, the spin borne on Co ions did not differ much from the values borne in undoped compounds, indicating a Yb$^{3+}$ substituting for a Co$^{3+}$.

We just demonstrated how the location of both Gd and Yb dopants which critically depend on the O partial pressure, influence the electronic structure of the host material. Now let us examine the implication of dopant’s location...
on the thermoelectric performance of Gd and Yb doped Na$_{1-x}$CoO$_2$ in terms of Seebeck coefficient ($S$), carrier concentration ($n$), conductivity ($\sigma$) and power factor (PF = $S^2\sigma$). The high-temperature Seebeck coefficient in Na$_{1-x}$CoO$_2$ can be explained by Koshibae’s equation \[47, 48\] for strongly correlated materials which is a modified form of Heikes formula \[49, 50\]:

\[
S (T \to \infty) = -\frac{k_B}{e} \ln \left[ \frac{g(\text{Co}^{4+}) n_{\text{Co}^{4+}}}{g(\text{Co}^{3+}) n_{\text{Co}^{3+}}} \right].
\] (7)

Here $k_B$ is the Boltzmann constant and $e$ is the electron charge, $g$ equals to the different possible ways in which electrons can be arranged in the orbitals of Co$^{3+}$ and Co$^{4+}$ ions, and $n$ is the concentration of a given species of Co. $g$ can be expressed as the product of spin degeneracy ($g_s$) and orbital ($g_o$) degeneracy: $g = g_s \cdot g_o$. $g_s$ equals to $2\zeta + 1$ where $\zeta$ is the ions’ total spin number while $g_o$ is the number of valid permutations for distributing the electrons across its orbitals. Assuming that Co ions take low spin state in Na$_{1-x}$CoO$_2$ ($\zeta = 0$ for Co$^{3+}$ and $\zeta = 1/2$ for Co$^{4+}$), we obtain $g(\text{Co}^{3+}) = 6$ and $g(\text{Co}^{4+}) = 1$. By substituting these values in the modified Koshibae’s formula for $S$ of an electron hopping from a Co$^{3+}$ ion to a Co$^{4+}$ ion, we obtain values of $S = 249 \mu$V K$^{-1}$ for Na$_{0.75}$CoO$_2$ and $S = 154 \mu$V K$^{-1}$ for Na$_{0.50}$CoO$_2$. It should be noted that Koshibae’s formula was obtained by solving the transport problem for a strongly correlated oxide using a Hubbard model at an infinite temperature \[51\]. The yielded results are, nonetheless, valid for doped Na$_{1-x}$CoO$_2$, as these compounds are generally intended for waste heat recovery at temperatures higher than ~700 K \[12\]. For further details see figure S4 of the supplementary information.

Furthermore, we can approximate the conductivity as a function of Co$^{4+}$ concentration by assuming that the carrier mobility remains 1.0 cm$^2$ V$^{-1}$ s$^{-1}$ for doped Na$_{1-x}$CoO$_2$ \[52\] for which full details are provided in table S4. This approximation is somehow conservative as dopants in Na layer are generally expected to improve carrier mobility slightly \[34\]. This approximation gives a conductivity value of $1.03 \times 10^3$ Ω$^{-1}$ cm$^{-1}$ for Na$_{0.75}$CoO$_2$ and $2.06 \times 10^3$ Ω$^{-1}$ cm$^{-1}$ for
Figure 4. Partial density of states of the most stable doping configurations in O poor environment (left column) and O rich environment (right column) for Gd doped Na$_{0.75}$CoO$_2$ (top panels) and Na$_{0.50}$CoO$_2$ (bottom panels). Blue, green and red lines represent Gd 4f, Co 3d and O 2p states, respectively.

Figure 5. Partial density of states of the most stable doping configurations in O poor environment (left column) and O rich environment (right column) for Yb doped Na$_{0.75}$CoO$_2$ (top panels) and Na$_{0.50}$CoO$_2$ (bottom panels). Purple, green and red lines represent Yb 4f, Co 3d and O 2p states, respectively.
Figure 6. (a) Seebeck coefficient ($S$) based on Koshibae’s equation, (b) conductivity ($\sigma$) and (c) the power factor in Na$_{1-x}$CoO$_2$ as a function of Co$^{4+}$ concentration. Green and pink arrows indicate the change in $S$ for cobalt site doping. The blue and red arrows indicate the change of $S$, $\sigma$ and PF for Na site doping.

Na$_{0.50}$CoO$_2$. The power factor, which is a parabolic function of $S$ and a linear function of $\sigma$, comes out as $6.392$ mW m$^{-1}$ K$^{-2}$ for Na$_{0.75}$CoO$_2$ and $4.912$ mW m$^{-1}$ K$^{-2}$ in Na$_{0.50}$CoO$_2$. These values are quite similar to measurements in single-crystal [53, 54] and epitaxial thin film Na$_{1-x}$CoO$_2$ [55]. The conductivity values, however, are an order of magnitude larger than those measured in polycrystalline samples indicating the significant role of carrier scattering at grain boundaries [56].

In O poor environment, Gd$_{\text{Int}}$ is the most stable configuration in both Na$_{0.75}$CoO$_2$ and Na$_{0.50}$CoO$_2$. Intertstitial Gd$^{3+}$ introduces three electrons that recombine with three holes of the host compound, reducing the concentration of Co$^{4+}$. As marked with red and blue arrows in figure 6(a), such a reduction in Co$^{3+}$ concentration increases $S$ to $388$ $\mu$V K$^{-1}$ in Na$_{0.75}$CoO$_2$:Gd$_{\text{Int}}$ and to $222$ $\mu$V K$^{-1}$ in Na$_{0.50}$CoO$_2$:Gd$_{\text{Int}}$. The reduction in Co$^{4+}$ concentration also decreases carrier concentration ($n$) and conductivity ($\sigma$). As marked with red and blue arrows in figure 6(b), Gd$_{\text{Int}}$ reduces $\sigma$ to $2.58 \times 10^2$ $\Omega^{-1}$ cm$^{-1}$ in Na$_{0.75}$CoO$_2$:Gd$_{\text{Int}}$ and to $1.29 \times 10^3$ $\Omega^{-1}$ cm$^{-1}$ in Na$_{0.50}$CoO$_2$:Gd$_{\text{Int}}$. As shown in figure 6(c), the power factor, decreases to $3.873$ mW m$^{-1}$ K$^{-2}$ for Na$_{0.75}$CoO$_2$:Gd$_{\text{Int}}$ while it increases to $6.367$ mW m$^{-1}$ K$^{-2}$ in Na$_{0.50}$CoO$_2$:Gd$_{\text{Int}}$. In O poor environment, Yb dopants replace an existing Na. In this case, each Yb dopant introduces two electrons. As a result, the reduction in Co$^{4+}$ concentration and conductivity is less dramatic than the case of Gd doping. For Na$_{0.75}$CoO$_2$:Yb$_{\text{Na1}}$, $S$, $\sigma$ and power factor, therefore, were calculated to be $322$ $\mu$V K$^{-1}$, $5.15 \times 10^2$ $\Omega^{-1}$ cm$^{-1}$ and $5.344$ mW m$^{-1}$ K$^{-2}$, respectively. For Na$_{0.50}$CoO$_2$:Yb$_{\text{Na2}}$, on the other hand, $S$, $\sigma$ and power factor, were calculated to be $198$ $\mu$V K$^{-1}$, $1.55 \times 10^3$ $\Omega^{-1}$ cm$^{-1}$ and $6.085$ mW m$^{-1}$ K$^{-2}$ respectively.

Gd$^{3+}$ and Yb$^{3+}$ dopants, when substituting for Co$^{4+}$ as in O rich environment, do not change the carrier (hole) concentration. However, they change the dynamics of spin entropy flow. As shown in figures 4(b), (d), 5(b) and (d), the $4f$ states of Gd and Yb dopants gravitate towards the bottom of the valence band hybridising with O 2$p$ and Co’s bonding $e_g$ states. The electric conduction and therefore the spin entropy flow is facilitated by the electrons hopping from a full $t_{2g}$ states of a Co$^{3+}$ ion to a singly vacant $t_{2g}$ states of a Co$^{4+}$ which are all located within ~1eV of the Fermi level. Consequently, Gd$_{\text{Co}}$ and Yb$_{\text{Co}}$, in practice, reduce the Co$^{3+}$ sites available for conduction, increasing the overall concentration of Co$^{4+}$. Taking the reduced number of Co$^{3+}$ sites into account, as marked with green and pink arrows in figure 6(a), according to Koshibae’s equation, $S$ is reduced to $241$ $\mu$V K$^{-1}$ for Na$_{0.75}$CoO$_2$ doped with Gd$_{\text{Co}}$ and Yd$_{\text{Co}}$ and to $142$ $\mu$V K$^{-1}$ for Na$_{0.50}$CoO$_2$ doped with Gd$_{\text{Co}}$ and Yd$_{\text{Co}}$. The carrier concentration, on the other hand, is not altered by Co side doping as the concentration of hole bearing Co$^{4+}$ does not change by either Gd$_{\text{Co}}$ or Yd$_{\text{Co}}$ doping. The net result for Co site doping that which is prevalent in O rich environment is, therefore, a net decrease in the power factor.

Earlier experiments have confirmed the possibility of doping in Na$_{0.50}$CoO$_2$ with Gd and Yb [23, 57]. In the case of Yb doping in Na$_{0.50}$CoO$_2$, synthesised through solid-state reaction, 5% Yb doping decreased $\sigma$ by ~25% compared to the undoped compound over the temperature range of 400 – 1000 K (form ~2.94 $\times$ 10$^2$ $\Omega^{-1}$ cm$^{-1}$ to 2.27 $\times$ 10$^2$ $\Omega^{-1}$ cm$^{-1}$). Yb doping, on the other hand, slightly increased $S$ from ~185 $\mu$V K$^{-1}$ to ~205 $\mu$V K$^{-1}$ at 800 K [23]. As a result, Yb doping increased the PF to ~1.5 mW m$^{-1}$ K$^{-2}$ from the ~1.2 mW m$^{-1}$ K$^{-2}$ of the undoped sample. The effect of Yb doping on the thermoelectric Na$_{0.50}$CoO$_2$ is in general agreement with our theoretical prediction. One, however, should note that, as shown in figure 6(c), the PF as a function of carrier concentration has a maximum of 6.416 mW m$^{-1}$ K$^{-2}$ at a Co$^{4+}$ concentration of 0.275. The hypothetical compound Na$_{0.725}$CoO$_2$ moves the PF towards that maximum.

The hypothetical compound Na$_{0.725}$CoO$_2$, synthesised through solid-state reaction, ~185 $\mu$V K$^{-1}$ and 6.085 mW m$^{-1}$ K$^{-2}$ at 800 K [23]. As a result, Yb doping increased the PF to ~1.5 mW m$^{-1}$ K$^{-2}$ from the ~1.2 mW m$^{-1}$ K$^{-2}$ of the undoped sample. The effect of Yb doping on the thermoelectric Na$_{0.50}$CoO$_2$ is in general agreement with our theoretical prediction. One, however, should note that, as shown in figure 6(c), the PF as a function of carrier concentration has a maximum of 6.416 mW m$^{-1}$ K$^{-2}$ at a Co$^{4+}$ concentration of 0.275. The hypothetical compound Na$_{0.725}$CoO$_2$ would have the maximum attainable power factor. This composition, however, above the convex hull of the Na$_{1-x}$CoO$_2$ phase diagram [58, 59]. As a result, altering Co$^{4+}$ concentration through doping in a stable Na$_{1-x}$CoO$_2$ composition is the only way to attain the maximum PF value. Consequently, electron doping, such as the case of Yb$_{\text{Na}}$ and Gd$_{\text{Int}}$, in the Na layer in Na$_{0.50}$CoO$_2$ moves the PF towards that maximum while electron doping in Na$_{0.75}$CoO$_2$ takes the thermopower away from this maximum.

Ca$_3$Co$_4$O$_9$ is another compound with many similarities to Na$_{1-x}$CoO$_2$ in which the Seebeck effect originates from the
spin entropy flow from Co$^{3+}$ to Co$^{4+}$ ions. Similar to our prediction for Gd and Yb doping in Na$_{0.50}$CoO$_2$, Gd doping at 10% in Ca$_3$Co$_4$O$_9$, Gd was found to decrease $\sigma$ from $\sim$100 $\Omega^{-1}$ cm$^{-1}$ to $\sim$67 $\Omega^{-1}$ cm$^{-1}$ and to increase $S$ from 125 $\mu$V K$^{-1}$ to 145 $\mu$V K$^{-1}$ at 400 K [60]. Similarly, $\sim$13% Yb doping in Ca$_3$Co$_4$O$_9$, Gd was found to decrease $\sigma$ to $\sim$45 $\Omega^{-1}$ cm$^{-1}$ which is half of the value of the undoped compound and to raise $S$ to $\sim$45 $\Omega^{-1}$ cm$^{-1}$ [61]. Judging from the combined effect on conductivity and Seebeck coefficient, these dopants, most likely, occupy a Ca site in calcium cobaltate.

Conclusions

Through density functional calculations with LDA + $U$ formalism, we showed that the formation energy of Gd and Yb dopants in Na$_{0.50}$CoO$_2$ and Na$_{0.50}$CoO$_2$ was critically sensitive to the synthesis conditions. In an oxygen poor environment, Gd and Yb dopants preferred to occupy a spot in the Na layer while in oxygen rich environment these dopants replaced a Co. Since Gd and Yb have a higher oxidation state than Na, when at Na layer, these dopants reduce the carrier concentration and the electric conductivity via electron–hole recombination and increase the Seebeck coefficient at the same time. The thermoelectric power factor, however, improves only for doped Na$_{0.50}$CoO$_2$ for which the increased Seebeck coefficient supersedes the reduction in the electric conductivity. When replacing a Co, Gd and Yb dopants reduce the Seebeck coefficient while leaving the electric conductivity unchanged resulting in a net reduction in the power factor.

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ORCID iDs

M Hussein N Assadi https://orcid.org/0000-0002-1559-3211

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