Exploring the possibility of enhancing the high figure-of-merit (\( > 2 \)) of \( \text{Na}_{0.74}\text{CoO}_2 \) by using combined experimental and theoretical studies

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Search of new thermoelectric (TE) materials with high figure-of-merit (ZT) is always inspired the researcher in TE field. Here, we present a combined experimental and theoretical study of TE properties of \( \text{Na}_{0.74}\text{CoO}_2 \) compound in high temperature region. The experimental Seebeck coefficient (S) is found to vary from 64 to 118 \( \mu \text{V/K} \) in the temperature range 300 – 620 K. The positive values of S are indicating the dominating p-type behaviour of the compound. The observed value of thermal conductivity (\( \kappa \)) is \( \sim 2.2 \text{ W/m-K} \) at 300 K. In the temperature region 300 – 430 K, the value of \( \kappa \) increases up to \( \sim 2.6 \text{ W/m-K} \) and then decreases slowly till 620 K with the corresponding value of \( \sim 2.4 \text{ W/m-K} \). To understand the experimental transport properties, we have carried out the theoretical calculations using DFT and DFT+\( U \) methods. The best matching between experimental and calculated values are observed when the calculation is done by chosen \( U = 4 \text{ eV} \) in DFT+\( U \). Calculations predict the half-metallic ferromagnetic ground state of the compound. By taking calculated S and electrical conductivity (\( \sigma \)) along with experimental \( \kappa \), we have optimized the ZT values up to 1200 K and the maximum value is found to be \( \sim 0.67 \) at 1200 K. Computational study suggests that the possibility of n-type behaviour of the compound which can lead to a large value of ZT at higher temperature region. Electron doping of \( \sim 5.1\times10^{20} \text{ cm}^{-3} \) is expected to give rise the high ZT value of \( \sim 2.7 \) at 1200 K. Using these temperature dependent ZT values, we have calculated the maximum possible values of efficiency (\( \eta \)) of thermoelectric generator (TEG) made by p and n-type \( \text{Na}_{0.74}\text{CoO}_2 \). The present study suggests that one can get the efficiency of a TE cell as high as \( \sim 11\% \) when the cold and hot end temperature are fixed at 300 K and 1200 K, respectively. Such high values of ZT and efficiency suggest that \( \text{Na}_{0.74}\text{CoO}_2 \) can be used as a potential candidate for high temperature TE applications.

Key words: Seebeck coefficient, electrical conductivity, thermal conductivity, electronic structure calculations, power factor figure-of-merit, efficiency.

I. INTRODUCTION

Thermoelectric (TE) materials convert the waste heat into useful electricity\(^1\) and are believed to play an important role in the future new energy-conversion system. The efficiency of TE materials is evaluated by a dimensionless parameter, figure-of-merit (ZT)\(^2\)

\[
ZT = \frac{S^2\sigma T}{\kappa}
\]  
(1)

where, S is Seebeck coefficient, \( \sigma \) is electrical conductivity, T is absolute temperature and \( \kappa (= \kappa_e + \kappa_{ph}) \) is thermal conductivity. For a good TE material, the value of ZT should be \( \geq 1 \)\(^2\). Therefore, for efficient TE materials we need to have high S and \( \sigma \) with low \( \kappa \). But, the realization of high ZT value is difficult, because all these three parameters (S, \( \sigma \) and \( \kappa \)) are interrelated to each other\(^2\). From the last few decades, many experimental and theoretical approaches have been used to improve the value of ZT.

Till now, the best commercially used TE materials available are bismuth (and lead) telluride and its alloys with highest ZT \( \sim 1 \) near the room temperature\(^3\). However, some of these materials are rare, costly and toxic. In addition, these materials can’t sustain at high temperature region. In this context, oxide materials have gained more attention in TE family due to their high temperature stability, low-cost, non-toxic, oxidation free and simple synthesis procedure. \( \text{Na}_{x}\text{CoO}_2 \) is one of the most studied TE candidate among the oxide materials in last two decades. The study of TE properties in \( \text{Na}_{x}\text{CoO}_2 \) was started when Terasaki \textit{et al.}\(^4\) reported a large thermopower (100 \( \mu \text{V/K} \) at 300 K) in \( \text{NaCo}_2\text{O}_4 \) in 1997. The spin entropy has been found to play an important role for this unusual large values of S in this system\(^5\). Na-site substitution effects on the thermoelectric properties of \( \text{NaCo}_2\text{O}_4 \) was studied by Kawata \textit{et al.}\(^6\). The attention in this compound was again stimulated by the discovery of superconductivity at 5 K in \( \text{Na}_{0.35}\text{CoO}_2\cdot1.3\text{H}_2\text{O} \)\(^7\). Further investigation of the S in \( \text{Na}_{x}\text{CoO}_2 \) has reported by Kaurav \textit{et al.}\(^8\) by varying the \( x \) values from 0.23 to 0.84.

A detailed experimental and theoretical TE study on \( \text{Na}_{x}\text{CoO}_2 \) has been carried out by many groups\(^9\) from last two decades. All these studies were done in low temperature region (0 – 300 K). A very few groups have been studied the TE properties of \( \text{Na}_{x}\text{CoO}_2 \) in high temperature region with poor and scattered data quality\(^10\). To the best of our knowledge, there are no such systematic study on TE properties of this compound available in high temperature region. Therefore, investigation of TE properties in this compound is required at elevated
temperature.

$Na_{1-x}CoO_2$ $(0.25 < x < 0.8)$ possess hexagonal symmetry with space group of 194: P63/mmc with two triangular CoO$_2$ layers per unit cell, has been reported by many groups. Magnetic ordering has been observed for $Na_{0.74}CoO_2$ with low transition temperatures of ~22 K. 

Computational approach always help in either searching the new materials or explaining the existing experimental results. In computational methods, density functional theory (DFT) is one of the most popular tools to predict the ground state electronic structure of the materials. In DFT, many exchange-correlation (XC) functionals have been developed for better approximations with their own merit and demerit. However, DFT is not capable of explaining the electronic structure of strongly correlated electron systems containing partially filled $d$ or $f$-band. In this context, DFT+U can be used, where on-site Coulomb interaction, $U$ takes the responsibility to overcome this problem. Therefore, the motivation of this work is up to what extent the experimentally observed TE properties of $Na_{0.74}CoO_2$ can be explained by DFT and DFT+U. Then by taking the best computational results, can we further improve the TE properties of the compound in high temperature region where performing our experiment is not accessible?

In this work, we have measured $S$ and $κ$ for $Na_{0.74}CoO_2$ in the temperature region 300 – 620 K. The values of $S$ were found to be ~64 – 118 μV/K and which increase linearly with temperature. Positive values of $S$ through-out the studied temperature range indicates the p-type behaviour of the compound. The observed values of $κ$ increase from 2.2 to 2.6 W/m-K in the temperature range 300 – 430 K and then decrease slowly up to 620 K with corresponding value of 2.4 W/m-K. In order to understand the experimentally observed transport properties, electronic structure calculations of this compound were carried out using DFT and DFT+U methods. Computational calculations predict the half-metallic ferromagnetic (FM) ground state of the compound. The temperature dependence of $S$ and $σ$ were also calculated using DFT and DFT+U, by varying $U$ from 2 to 5 eV and compared with experiment. The best matching between experimental and calculated values are observed when the value of $U$ was taken to be 4 eV along with DFT. Then, based on the understanding of computational results, we have optimized the ZT value from 300 to 1200 K. The maximum ZT value is found to be ~ 0.67 at 1200 K. The possibility of n-type behaviour of this compound was also investigated with the help of computational results which can lead to high ZT value in high temperature region. Electron doping of $\sim 5.1 \times 10^{20}$ cm$^{-3}$ gives the high ZT value of $\sim 2.7$ at 1200 K. Finally, we have calculated the temperature dependent efficiency ($η$) of TEG which is made by p and n-type $Na_{0.74}CoO_2$ using the calculated ZT values. The maximum possible value of $η$ which was taken from average of p and n-type compound can be obtained as $\sim 11\%$ when the cold and hot end temperatures were fixed to be at 300 K and 1200 K, respectively. The high temperature values of ZT and efficiency suggest that $Na_{0.74}CoO_2$ can be used as a promising TE candidate for high temperature applications in power plant utility.

II. EXPERIMENTAL AND COMPUTATIONAL DETAILS

$Na_{0.74}CoO_2$ sample was prepared by solid state reaction, more details of synthesis procedure and characterization can be found in Ref. [27]. The measurements of $S$ and $κ$ were performed in the temperature range 300 – 620 K by using the home-made experimental setup. The circular pellet of 8 (±0.1) mm diameter with 1 (±0.02) mm thickness was used for $S$ and $κ$ measurements.

To examine the experimentally observed transport properties of the sample, we have done electronic structure calculations with density functional theory (DFT). In the calculations, full-potential linearized augmented plane wave (FP-LAPW) method is used which is implemented in WIEN2k code. The PBEsol is used as an exchange correlation functional within generalized gradient approximation (GGA). The lattice parameters of $a = b = 2.823$ Å & $c = 10.933$ Å and space group: P63/mmc (no. 194) were used for the ground-state self-consistent calculations. The muffin-tin sphere radii for Co, Na and O atoms were fixed to be 1.79, 2.09 and 1.54 Bohr, respectively. The on-site coulomb interaction strength, $U$ was taken from 2 to 5 eV in DFT+U method. A k-mesh of size $3 \times 15 \times 8$ was used for the calculations. The criteria for calculating the total ground state energy of the compound in self-consistency cycle was set to be less than 0.1 mRy. For such a vacant compound minimization of internal parameters have done to relax the system. Force convergence criteria was set to be 1 mRy/Bohr during the minimization of internal parameters. The temperature dependence of transport properties ($S$ and $σ$) are calculated by using BoltZTraP package, which is interfaced with WIEN2k. A k-mesh of size $19 \times 75 \times 43$ was used for calculating the transport properties of the compound.

III. RESULTS AND DISCUSSION

A. Experimental transport properties

Fig. 1(a) shows the experimentally observed Seebeck coefficients ($S$) of $Na_{0.74}CoO_2$ compound as a function of temperature. The measured value of $S$ is ~64 μV/K at 300 K which is found to give a good agreement with reported values for $Na_{0.74}CoO_2$. As the temperature increases, the values of $S$ also increase almost linearly up to the highest temperature studied. At 620 K, the value of $S$ is found to be ~118 μV/K. The positive values of $S$ are observed in the full temperature range indicating the dominating p-type behaviour of the compound. The
value of \( S \) at 620 K is almost double the value at room temperature. This increasing nature of \( S \) vs \( T \) suggests that \( \text{Na}_{0.74}\text{CoO}_2 \) can be used in high temperature region to get a higher power factor (\( S^2 \sigma \)).

Temperature dependence of thermal conductivity (\( \kappa \)) of the sample in the temperature region 300 – 620 K is displayed in Fig. 1(b). The observed value of \( \kappa \) is \( \sim 2.2 \) W/m-K at 300 K, which found to give a good match with reported value by Mallick et al.\(^{18,19} \). In the temperature range 300 – 430 K, the value of \( \kappa \) increases up to \( \sim 2.6 \) W/m-K at 430 K. As the temperature increases further from 430 K, the value of \( \kappa \) is decreasing slowly and it’s value is found to be \( \sim 2.4 \) W/m-K at 620 K. These low values of \( \kappa \) under the studied temperature range help to increase the ZT value for this compound.

### B. Force minimization and electronic structure calculations

The primitive cell of \( \text{Na}_{0.74}\text{CoO}_2 \) compound contains 10 atoms to form a lattice with the Wyckoff positions: Co at 2a(0, 0, 1/2), Na1 at 2b(0, 0, 1/4), Na2 at 2c(2/3, 1/3, 3/4) and O at 4f(1/3, 2/3, 0.0913). But, the formula unit of our synthesized compound contains one Co atom, 0.23 Na1 atom, 0.51 Na2 atom and two O atoms. Therefore, fraction of Na atom is needed to be removed from structure for doing the self-consistent field (SCF) calculations. But, the fraction of atom is meaningless. Thus, we have created the supercell and removed the unwanted Na atoms from the structure file. Here, it is important to note that there are so many combinations for removing Na atoms. It is found that, every combination is giving almost same results once we relax the system by giving the force minimization criteria in SCF calculations. Therefore, care should be taken to do the electronic structure calculations for such a vacant system.

To know the ground state of the compound, the SCF calculations for non-magnetic (NM) and ferromagnetic (FM) phases were performed within density functional theory (DFT). The selected bond distances and angles are shown in Table I corresponding to NM and FM results along with experiment. Fig. 2 shows the crystal structure of the compound of \( 2\times1\times1 \) supercell with indexing the atoms for supporting of Table I. From the table it is seen that all the \( \text{Co} – \text{O} \) bond lengths corresponding to NM and FM phases are different from that of experiment which may be due to supercell calculations. The average distance of \( \text{Co} – \text{O} \) for NM and FM are 1.903 Å and 1.904 Å, respectively and which are very much close to experimental value of 1.912 Å. The average bond angle of \( \text{Co} – \text{O} – \text{Co} \) corresponding to NM and FM phases are 95.51 deg and 95.49 deg, respectively and which are also closely matching with experimental value of 95.22 deg. The value of total energy in the case of FM solution is found to be \( \sim 7.5 \) meV/f.u. lower than that of NM solution. This result suggests that the ground state of this compound is FM with low transition temperature (\( T_c \)) which is accordance with the reported results.\(^{19,20,23} \)

The calculated magnetic moment of this compound is also found to be \( \sim 1.12 \mu_B \)/f.u., which gives the good agreement with the experimentally observed values of magnetic moment.\(^{20} \) The major contribution in magnetic moment comes from Co atom which is almost 80% of the total value. In order to explain the experimentally observed transport properties of this compound, the density of states (DOS) calculations are carried out corresponding to NM and FM phases.

Fig. 3 exhibits the DOS plots corresponding to NM and FM phases of \( \text{Na}_{0.74}\text{CoO}_2 \). The dashed line at 0 eV represents the Fermi level, \( E_F \) of the compound. Fig. 3(a) shows the total DOS (TDOS) for NM phase of the compound within DFT. The value of DOS is found to be \( \sim 3.2 \) states/eV/f.u. at Fermi level from the figure. This considerable amount of DOS at \( E_F \) may be considered as a signature of FM ground state of the compound on the basis of Stoner theory. TDOS for FM phase is also calculated under DFT, which is shown in Fig. 3(b). The contribution of DOS corresponding to spin-up and spin-down channels is asymmetric. From the figure it is observed that spin-down channel is giving finite DOS of \( \sim 2 \) states/eV/f.u. at \( E_F \), whereas spin-up channel gives
TABLE I: Selected bond lengths and angles corresponding to non-magnetic (NM) and ferromagnetic (FM) phases of Na$_{0.74}$CoO$_2$ along with experiment.

| Type of bond         | Bond length (Å) | NM   | FM   | Experiment |
|----------------------|-----------------|------|------|------------|
| Co(1) - Co(2)        | 2.8232          | 2.8231| 2.8237|            |
| Co(1) - O(1)         | 1.9207          | 1.9294| 1.9116|            |
| Co(1) - O(2)         | 1.8810          | 1.8822| 1.9116|            |
| Co(1) - O(3)         | 1.9256          | 1.9261| 1.9116|            |
| Co(1) - O(4)         | 1.8658          | 1.8655| 1.9116|            |
| Co(2) - O(1)         | 1.9313          | 1.9306| 1.9116|            |
| Co(2) - O(2)         | 1.8868          | 1.8875| 1.9116|            |

FIG. 2: Crystal structure of Na$_{0.74}$CoO$_2$ for 2×1×1 supercell.

the finite band gap of ∼ 0.9 eV. Therefore, this result predicts the half-metallic ground state of the compound.

In order to explain the experimental results in better way, inclusion of on-site Coulomb interaction for Co 3$d$ electrons in DFT+U calculations is required. The TDOS has calculated for different values of $U$ varied from 2 to 5 eV. Then the value of $U$ is chosen to be 4 eV by comparing the calculated transport results with experiment. This value of $U$ is found in good agreement with the reported value by Wissgott et al.$^{24}$ Fig. 3(c) shows the calculated TDOS plot of the compound corresponding to FM phase under DFT+U method. Inclusion of $U$, generally increase the separation between occupied and unoccupied states and transfers the spectral weight between the energy positions. Due to which, gap in the energy region ∼ -1.85 to -1.33 eV vanishes. From the figure, it is also seen that the features of DOS in dn-channel around $E_F$ is different from that of DFT DOS. Therefore, all these results suggest that DFT+U calculation is expected to give the different transport properties over DFT for this compound.

In order to know the contribution in TDOS from different atomic orbitals, we have calculated the partial DOS (PDOS) for constituent atoms of Na$_{0.74}$CoO$_2$. From the calculations, it is observed that the electronic contributions near the Fermi level comes from Co 3$d$ and O 2$p$ orbitals mainly with negligibly small contribution from Na 3$s$ orbital. Hence, here we present the PDOS corresponding to Co 3$d$ and O 2$p$ orbitals, which is shown in fig. 3(d). From the figure, it is clear that at $E_F$, a quite good amount of DOS in dn-channel is observed. These values are found to be ∼ 1.31 states/eV/atom and ∼ 0.45 states/eV/atom for Co 3$d$ and O 2$p$ orbitals, respectively. Thus, due to metallic nature of dn-channel, the electrons from hybridized Co 3$d$ and O 2$p$ states are expected to give the large contribution in electrical conductivity ($\sigma$). In specific, the contributions in DOS from Co 3$d$ orbitals is almost triple than that of O 2$p$ orbitals in spin-dn channel at $E_F$. This suggests that Co 3$d$ orbitals take the main responsibility in $\sigma$ values. For up-channel, from the edge of the valence band (VB), peaks are associated at ∼ −0.65 eV for both Co 3$d$ and O 2$p$ orbitals and the values of DOS are found to be ∼ 3.58 states/eV/atom and ∼ 1.75 states/eV/atom, respectively. Therefore, due to semiconducting nature of up-channel, large values of $S$ and small values of $\sigma$ are expected from Co 3$d$ and O 2$p$ orbitals. Here, one should conclude that the major contribution in S and $\sigma$ come from Co 3$d$ mainly.

C. Calculated transport properties

The temperature dependence of $S$ and $\sigma$ are calculated for spin-up and spin-dn channels using BoltZTraP package.$^{23}$ The total $S$ and $\sigma$ values are needed to be calculated from up and dn-channels to analyze the experimental results. Here, two current model is employed to calculate the total $S$ from the values of spin-up and spin-dn channel. In this model, total S can be expressed as the following equation

$$S = \frac{(\sigma^\uparrow S^\uparrow + \sigma^\downarrow S^\downarrow)}{(\sigma^\uparrow + \sigma^\downarrow)} \quad (2)$$

where, $\sigma^\uparrow$ and $\sigma^\downarrow$ are the electrical conductivities and $S^\uparrow$ and $S^\downarrow$ are the Seebeck coefficients of up and dn-channels, respectively. Using Eqn 2, the values of S are calculated within DFT and DFT+U methods. At $\mu = 0$ eV (Fermi level), the calculated values of S are ∼ −15 to 19 $\mu$V/K at 300 K using DFT and DFT+U and which are quite far away from the experimental value of ∼ 64 $\mu$V/K. This result suggests that the $\mu$ value may not be suitable for calculating S, which can be understood by the following ways. As we know that, maintaining the oxygen stoichiometry is always a difficult task in oxide materials. In addition, the evaporation of Na during the sample preparation is the another issue in the present compound.
FIG. 3: Total density of states (TDOS) of (a) non-magnetic (NM) phase using DFT, (b) ferromagnetic (FM) phase using DFT and (c) FM phase using DFT+U; (d) Partial DOS (PDOS) of FM phase using DFT+U.

TABLE II: Calculated Seebeck coefficients (S) at different temperature by using DFT and DFT+U. The average of absolute deviation of S from experiment is also shown, where n is the total number of data points at different temperature. (Here, S is in µV/K unit).

| Methods               | S at 300 K | S at 400 K | S at 500 K | S at 600 K | S at 620 K | (∑|S_exp − S_cal|)/n |
|-----------------------|------------|------------|------------|------------|------------|----------------------|
| Experiment            | 64.08      | 80.98      | 99.30      | 116.18     | 118.21     | —                    |
| DFT                   | 58.12      | 81.47      | 98.80      | 111.43     | 113.54     | 2.03                 |
| DFT+U (U = 2 eV)      | 59.05      | 81.35      | 98.60      | 111.00     | 113.01     | 2.06                 |
| DFT+U (U = 3 eV)      | 57.88      | 79.40      | 97.05      | 110.21     | 112.39     | 3.45                 |
| DFT+U (U = 4 eV)      | 64.43      | 82.75      | 99.55      | 112.96     | 115.23     | 1.41                 |
| DFT+U (U = 5 eV)      | 59.16      | 78.68      | 96.35      | 109.90     | 112.11     | 3.82                 |

These two factors may lead to change in µ value for the compound. Therefore, finding out the µ value at 300 K for calculating the S values is required to get a best matching with experiment. We found that at µ = 143, 182, 198, 220 and 231 meV, the calculated values of S are ~ 58 (DFT), ~ 59 (U = 2 eV), ~ 58 (U = 3 eV), ~ 64 (U = 4 eV) and ~ 59 (U = 5 eV) µV/K, respectively at 300 K and give the best match in each case. Using these µ values, we have calculated S in the temperature region 300 − 620 K as shown in Table 2. The average of absolute deviation of calculated S from experiment are also shown in the table. It is seen from the table that the lowest deviation is observed when S was calculated using U = 4 eV. Fig. 4 shows the calculated values of S using DFT and DFT+U (U = 4 eV) along with experiment. The calculated S values using DFT is deviating below ~ 360 K and above ~ 500 K from the experimental data which may be due to DFT is not able to give a proper DOS around the Fermi level for this compound as we have seen in DOS plots. From the figure it is clearly seen that the calculated values of S (using U = 4 eV) are giving good match with experiment throughout the studied

FIG. 4: Comparison of experimental and calculated (using DFT and DFT+U) values of Seebeck coefficient (S) as a function of temperature.
calculations, we used \( U = 4 \) eV can be used to study the temperature dependence of spin-up and spin-down channels. According to two-current model, the change in \( S \) with \( \mu \) is calculated at different temperature using \( U = 4 \) eV, as shown in Fig. 5 and which is used in finding out the \( \mu \) value for calculating the temperature dependence of \( S \). From the figure (left inset) it is clear that the positive values of \( S \) are seen at \( \mu \approx 220 \) meV for all the studied temperatures which is indicating the p-type behaviour of the compound and which is in accordance with our experimental results. Therefore, \( U = 4 \) eV can be used to study the temperature dependence of transport properties of \( \text{Na}_{0.74}\text{CoO}_2 \). For rest of the calculations, we used \( U = 4 \) eV and \( \mu = 220 \) meV in this work.

The temperature dependence of \( \sigma \) is also calculated for up and down channels. According to two-current model, the total \( \sigma \) can be calculated by the sum of \( \sigma \) of spin-up and spin-down channels and expressed as:

\[
\sigma = \sigma^\uparrow + \sigma^\downarrow
\]

The values of \( \sigma \) are calculated using Eqn. 3. But, we got \( \sigma^\uparrow \) (and \( \sigma^\downarrow \)) per relaxation time \( (\tau) \) from calculation. Therefore, the value of \( \tau \) is needed to be calculated to get an actual \( \sigma \). Comparing the reported values of \( \sigma \) \((3.45 \times 10^4 \ \Omega^{-1} \ \text{m}^{-1})\) at 300 K by Altin et al\textsuperscript{14} with calculated \( \sigma/\tau \), we have calculated the \( \tau \) value as \( 0.7 \times 10^{-14} \) s. This calculated value of \( \tau \) at RT is in the typical range of \( 10^{-14} - 10^{-15} \) for metals and semiconductors\textsuperscript{15} Then this constant value of \( \tau \) is used to calculate the \( \sigma \) in the temperature region 300 – 620 K as shown in Fig. 6 and also used for rest of the calculations in the present work. From the figure it is seen that the values of \( \sigma \) decrease up to \( \sim 420 \) K. After 420 K, these values are increasing up to 620 K with the corresponding value of \( 3.52 \times 10^4 \ \Omega^{-1} \ \text{m}^{-1} \).

**FIG. 5:** Change in Seebeck coefficient \((S)\) with chemical potential at different temperature using DFT\(+U\) (= 4 eV).

**FIG. 6:** Calculated values of electrical conductivity \((\sigma)\) as a function of temperature using DFT\(+U\) (= 4 eV).

**D. Power factor, figure-of-merit and efficiency**

To see the applicability of \( \text{Na}_{0.74}\text{CoO}_2 \) in TE world, we have calculated the power factor \((PF)\) with \( \mu \) at different temperature which is shown in Fig. 7. The dotted line at 0 eV denotes the Fermi level, \( E_F \) of the compound. Around the \( E_F \), the maximum PF is observed at \( \sim 280 \) meV for p-type behaviour with the corresponding values of \( \sim 4.2 \mu \text{WK}^{-2}\text{cm}^{-1} \) and \( \sim 10.5 \mu \text{WK}^{-2}\text{cm}^{-1} \) for 300 K and 1200 K, respectively. Here, it is important to note that experimental \( S \) and \( \sigma \) was matched with calculated values at \( \mu \approx 220 \) meV. Therefore, this calculation of PF suggest that small amount of doping may gain the capability in TE application of \( \text{Na}_{0.74}\text{CoO}_2 \).

By using the experimentally measured \( S \) and \( \kappa \) values with calculated \( \sigma \), we have computed the figure-of-merit \((ZT)\) using Eqn. 1 as given in Fig. 8(a) in the temperature region 300 – 620 K. The values of \( ZT \) increase with increasing of temperature. The observed value of \( ZT \) at 300 K is found to be \( \sim 0.02 \), whereas it reaches \( \sim 0.13 \) at 620 K. These values of \( ZT \) give good agreement with the reported values by Mallick et al\textsuperscript{18} The \( ZT \) value at 620 K is \( \sim 7 \) times larger than that of room temperature value. This result suggests to give an attention in high temperature TE application of this compound. Here, it is important to note that there is a scope to further improve the value of \( ZT \) by doping to achieve \( \mu \approx 280 \) meV, where PF is maximum (Fig. 7). By taking these values of PF along with experimental \( \kappa \) values, we have calculated \( ZT \) values in the temperature region 300 – 1200 K which is also presented in Fig. 8(a). The calculated value of \( ZT \) at 300 K is \( \sim 0.05 \), whereas it is found to be \( \sim 0.67 \) at 1200 K. In the full temperature region, \( ZT \) values are increasing monotonically. The values of \( ZT \) at high temperature are large enough to be used in high temperature
Till now, our entire discussion was on TE properties of p-type Na$_{0.74}$CoO$_2$. As we know that for making the thermoelectric generator (TEG), we need both p-type and n-type materials. Therefore, for the sake of curiosity, we examined the DOS plot to see the possibility for making this compound as n-type. If we observe the DOS plot of Fig. 3(c), we can see that by small amount of doping one can reach in semiconductor region (which starts at $\sim 385$ meV) as we are already at 220 meV above the E$_F$. Now, by doping of electrons one can make this compound as n-type as shown in Fig. 5 (right inset). Temperature dependence of PF are calculated in n-type region to find out the maximum value as shown in Fig. 7. From the figure, it is found that the maximum PF can be obtained at $\sim 2160$ meV, which corresponds to the electron doping of $\sim 5.1 \times 10^{20}$ cm$^{-3}$. At this doping level, the temperature dependence of S and $\sigma$ are calculated in temperature region 300 – 1200 K as shown in Fig. 9(a) and 9(b), respectively. The negative values of S in the full temperature region indicate the dominating n-type behaviour of the compound. By taking these values of S and $\sigma$ along with experimental $\kappa$, we have estimated the ZT values in the temperature region 300 – 1200 K which are presented in Fig. 8(b). The values of ZT at 300 K and 1200 K are found to be $\sim 0.1$ and $\sim 2.7$, respectively. At this stage, it is important to note that the values of ZT are calculated using the extrapolated experimental $\kappa$ values measured for p-type Na$_{0.74}$CoO$_2$. Here, it should be is noticed that the constant $\tau$ value calculated at 300 K was used for calculating the temperature dependence of $\sigma$. But, $\tau$ is temperature dependent quantity which
FIG. 9: Calculated values of (a) Seebeck coefficients and (b) Electrical conductivity of n-type Na$_{0.74}$CoO$_2$ in the temperature region 300 – 1200 K using DFT + $U$ (= 4 eV).

may affects the $\sigma$ values. By considering the temperature dependence of $\tau$ and correction in $\kappa$ at high temperature, we believe that one may still get ZT value $\approx 2$ at 1200 K, if this compound is synthesized with suitable n-type doping as mentioned. Therefore, high values of ZT of this compound in high temperature region deserved attention of the community in TE world.

Finally, we have calculated the maximum possible efficiency of TEG which is supposed to be made by p and n-type Na$_{0.74}$CoO$_2$ as shown in Fig. 10. Here, the cold end temperature ($T_c$) was kept constant at 300 K, whereas the hot end temperatures ($T_h$) were varied from 300 to 1200 K. The segmentation method was employed to calculate the efficiency as implemented by Gaurav et al. In this method, the efficiency of every segment is calculated by the following expression.

$$\eta_i = \frac{\Delta T}{T + \frac{\Delta T}{2}} \frac{\sqrt{1 + ZT} - 1}{\sqrt{1 + ZT} + \frac{\Delta T}{2}}$$

where $\Delta T$ and $T$ is the temperature difference and average temperature of each individual segment, respectively. First of all, we will discuss the efficiency of p-type Na$_{0.74}$CoO$_2$ and then n-type. In the temperature region 300 – 1200 K, the total number of segments ($n$) were calculated to be 90 by taking $\Delta T = 10$ K ($n = \frac{T_h - T_c}{\Delta T}$). For the first segment, using the value of $\Delta T = 10$ K, $T$ = 305 K and $ZT$ = 0.0556 in Eqn 4, we get $\eta_1 = 0.00044$. Similarly, we can calculate the efficiency of every consecutive segment up to $\eta_{90} = 0.00106$. By using these segmented efficiencies, we can calculate the overall efficiency by using the following formula

$$\eta_{overall} = 1 - (1 - \eta_1)(1 - \eta_2).........(1 - \eta_n)$$

In order to calculate $\eta_{overall}$ at $T_h$ = 400 K, 500 K, and 1200 K, we have taken the number of segments, $n = \frac{T_h - 300}{10} = 10, 20, ....$ and 90, respectively, whereas cold end temperature was kept fixed at 300 K. From Fig. 10, the maximum efficiency is found to be $\sim 6\%$ at $T_h = 1200$ K for p-type Na$_{0.74}$CoO$_2$. Similarly, the maximum possible efficiencies of n-type Na$_{0.74}$CoO$_2$ are calculated using Eqn. 4 which is also shown in Fig. 10. The maximum efficiency observed at 1200 K is $\sim 16\%$. The average of maximum efficiency of TEG made by p and
n-type Na$_{0.74}$CoO$_2$ is found to be $\sim 11\%$ at $T_h = 1200$ K. This value of efficiency is more than the value of TEG made by Bi$_2$Te$_3$, which is commercially used in low temperature region.\textsuperscript{45} Therefore, on the basis of studied ZT and efficiency, we propose Na$_{0.74}$CoO$_2$ compound is an efficient TE material. Thus, a rigorous effort should be done in synthesizing the n-doped Na$_x$CoO$_2$ compound.

\section*{IV. CONCLUSIONS}

In conclusion, the temperature dependence of TE properties (S and $\kappa$) of Na$_{0.74}$CoO$_2$ compound was measured in the temperature region 300 – 620 K. The observed values of S were found to be $\sim 64 – 118 \mu$V/K in the temperature region 300 – 620 K. The positive values of S indicate the dominating p-type behaviour of the compound. Low values of $\kappa$ (2.2 – 2.6 W/m-K) are observed for this compound which help to increase the ZT value. In order to understand the experimental results, ground state electronic structure calculations were carried out using DFT and DFT+U methods. The calculations predict the half-metallic ground state with FM phase of the compound. T vs S (and $\sigma$) were calculated using DFT and DFT+U and compared with experimental values. DFT+U is giving best match with experiment when the value of $U$ was chosen to be 4 eV. Then, we have estimated the ZT value up to 1200 K on the basis of computational understanding. The maximum value of ZT is found to be $\sim 0.67$ at 1200 K. Computational results suggest to find out the n-type behaviour of the compound which leads to give the high ZT value of $\sim 2.7$ at 1200 K with electron doping of $\sim 5.1 \times 10^{20}$ cm$^{-3}$. Finally, the maximum possible values of $\eta$ of TEG made by p and n-type Na$_{0.74}$CoO$_2$ were calculated as a function of hot end temperature. The maximum possible value of efficiency is found to be $\sim 11\%$ by fixing the cold and hot end temperature at 300 K and 1200 K, respectively. The calculated values of ZT and efficiency suggest to use this compound as a promising TE candidate for high temperature applications.

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