Enthalpy of Formation of Na$_x$CoO$_2$ and (Na, Mg)$_x$CoO$_2$ Systems: A First Principle Calculation Study

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Abstract. Enthalpy of formation of Na$_x$CoO$_2$ (NCO) compounds with 0 < x < 1 and partially substituted Na$^+$ ions with Mg$^{2+}$ ions, (Na, Mg)$_x$CoO$_2$ (NMCO) has been calculated using full potential-linear augmented plane wave method within density functional theory. The enthalpy of formation of NCO was found to decrease as sodium concentration, x increases. We found that the enthalpy of formation decreases more rapidly in region of 0 < x < 0.55 and slower in 0.55 < x < 1, which is indicating the presence of two different stability region against sodium concentration. The substitution of Mg$^{2+}$ into Na$^+$ sites decreases the enthalpy of formation of NCO compound and suggests Mg$^{2+}$ substitution could increase the stability of NCO compound. The Mg$^{2+}$ substitution also affect the lattice parameters. In the electronic structure, Mg$^{2+}$ substitution is found to lower the position of unfilled Co-3d band for about 0.2 eV compared to the NCO compound. The computational results also indicate that the Mg$^{2+}$ substitution will not affect Seebeck coefficient especially at high temperature.

1. Introduction
The layered sodium cobaltate compound of Na$_x$CoO$_2$ has received much attention due to their interesting properties such as superconducting properties in hydrated sodium cobaltate [1], and its potential application as thermoelectric devices [2] and sodium-ion batteries [3]. As thermoelectric devices, Na$_x$CoO$_2$ has large thermoelectric power of ~90 μV/K, low thermal conductivity and low electrical conductivity [4]. Those properties depend on the doping level or Na concentration in the crystal. For the sodium battery application, the stability of the Na$_x$CoO$_2$ compound with different Na concentration is important to be studied and further improvement in the structural stability is strongly expected.

Thermodynamic stability of materials could be studied experimentally and computationally. The thermodynamic stability of Na$_x$CoO$_2$ compounds have been studied experimentally by measuring the standard molar enthalpy of formation from Na concentration, x = 0.1 to 0.9 [5]. The enthalpy of formation could be calculated also using first principle calculation method based on the density functional theory (DFT) [6]. The computational method could be used to predict the properties materials under various conditions. The computational results could be used as a guide for experimental works as well as to explore broader applications.

In this paper, we report on our computational study results on the structural, thermodynamic, electronic structure and transport properties of the Na$_x$CoO$_2$ and (Na, Mg)$_x$CoO$_2$ compounds. In the (Na, Mg)$_x$CoO$_2$ compound, we studied the effect of Mg substitution on Na site to the properties of sodium cobaltate compound.
2. Computational Details

The DFT calculations were performed using WIEN2K package, which is a first principle calculation method using full potential-linearized augmented plane waves (FP-LAPW) [7]. We used Perdew-Burke-Ernzerhof generalized gradient approximation (PBE-GGA) [8] for the exchange correlation potential. In order to simulate the variation of Na content, we created 2x2x1 supercell and it would provide 8 independent Na sites. The k-point sampling was performed in the regular Monkhorst-Pack grid of 7x7x3 [9] and the maximum modulus of reciprocal lattice vector, $R_{\text{MT}}K_{\text{max}} = 7$. The muffin-tin radii ($R_{\text{MT}}$) for each atom are 1.60 for Na, 1.91 for Co, 1.64 for O and 2.10 for Mg. For (Na, Mg)$_x$CoO$_2$ system, we replaced one Na atom with one Mg atom for each x value and it simulated the composition of (Na, Mg)$_x$CoO$_2$.

The crystal structure of Na$_x$CoO$_2$ adopts hexagonal lattice system with P$_{6/m}$mc space group [10]. These structural data were used for the calculation and then were optimized before we proceed to calculate the total energy, density of states, electronic structure, and enthalpy of formation. The distribution of the charge in the cobalt atoms were calculated using atom in molecule (AIM) package and the transport properties were calculated using Boltztrap program [11].

3. Results and Discussions

The optimized lattice parameters of a and c for the Na$_x$CoO$_2$ (NCO) and (Na, Mg)$_x$CoO$_2$ (NMCO) compounds were shown in figure 1, together with the experimental results from Phapale, et al [5]. The lattice parameter a increases continuously as the Na concentration increases in agreement with the experimental result especially in the low Na concentration region. The substitution of Mg$^{2+}$ would enlarge the lattice parameter. Meanwhile, the optimized lattice parameter c has different behavior. For low Na concentration, it increases up to $x = 0.55$ and then decreases as Na concentration increases. It is very different with the experimental results, which was found to decrease continuously as Na concentration increases. This could be attributed to the larger repulsive force between the CoO$_2$ layers in the synthesized samples than predicted by the calculation results. The Mg substitution will reduce the lattice parameter c. Our calculation results indicate that at low Na concentration, the introduction of Na between the CoO$_2$ layers will increase the lattice parameter c and when $x$ larger than 0.55, the interaction between positively charge Na$^+$ and negative CoO$_2$ layers leads to the decreasing of lattice parameter c.

![Figure 1](image.png)

**Figure 1.** Calculated lattice parameters of Na$_x$CoO$_2$, (Na, Mg)$_x$CoO$_2$ and experimental results from ref. 5. (a) Lattice parameter-a. (b) Lattice parameter-c.
Figure 2. Plot of enthalpy formation of Na$_x$CoO$_2$ and (Na, Mg)$_x$CoO$_2$ against Na concentration.

The enthalpy of formation of NCO compound was calculated using formula: \( \Delta H_f = E_{\text{Total}}(\text{Na}_x\text{CoO}_2) - xE_{\text{Na}} - E_{\text{Co}} - 2E_{\text{O}} \), where \( E_{\text{Total}}(\text{Na}_x\text{CoO}_2) \) is the total energy of NCO system from the DFT calculation results. \( E_{\text{Na}} \) and \( E_{\text{Co}} \) is the total energy of the crystalline sodium and cobalt and calculated using the same procedure as the NCO. For the oxygen, we use the same calculation program and exchange correlation potential, but it is calculated in the periodic system with separation between oxygen molecules more than 10 Å. The enthalpy of formation for NMCO was calculated with the same procedure as the NCO compound. The enthalpy of formation of NCO and NMCO compounds were shown in figure 2. In general, the enthalpy of formation of the NCO compounds decreases as the Na concentration increases. However, the calculation predicted rapid decreasing up to \( x = 0.55 \) and then followed by slow decreasing. This indicated that there are two stability region in the NCO compound and the more stable compound is with Na concentration higher than 0.55. The Mg$^{2+}$ substitution on Na$^+$ sites will lower the enthalpy of formation value. The enthalpy of formation of NMCO was about 60 kJ/mol lower than the enthalpy of formation of NCO. This result suggests that the Mg$^{2+}$ substitution will increase the stability of the NCO compound.

Figure 3. (a) Total density of states of Na$_{0.875}$CoO$_2$. (b) Total density of states of (Na, Mg)$_{0.875}$CoO$_2$ with density of states of Mg (blue color).
We would like to study the effect Mg$^{2+}$ substitution at the Na sites further. Although, we have calculated the density of states and electronic structure of all composition, here, we only show the density of states of Na$_{0.875}$CoO$_2$ and (Na, Mg)$_{0.875}$CoO$_2$ compounds in figure 3. That compounds represent the NCO compound in the more stable region. The density of states consists of the contribution of Co-3d states around the Fermi level. Those Co-3d states are separated around 1 eV between the occupied and unoccupied Co-3d states. From -1.9 eV to 6.9 eV, it is dominated by the contribution of filled O-2p states. The empty Na-3s states are found at above 3.7 eV. For the (Na, Mg)$_{0.875}$CoO$_2$ compounds, the Mg-3s states are clearly seen between the Co-3d and Na-3s states in the energy range of 2.4 to 3.6 eV. The substitution of Mg$^{2+}$ ions also slightly shifts the unoccupied Co-3d states closer to the Fermi level. The lowest unoccupied states of Co-3d located at around 0.8 eV above the Fermi level.

![Figure 4](image_url)

Figure 4. (a) Band structure of Na$_{0.875}$CoO$_2$. (b) Band structure of (Na, Mg)$_{0.875}$CoO$_2$.

The electronic structure of NCO and NMCO compounds are shown in figure 4. The band structure of NCO and NMCO compounds are similar up to 2 eV, which are contributed from O-2p and Co-3d. At above 3.5 eV and for the NCO compound, dispersive band structure was observed and it is contributed by the empty Na-3s states. For the NMCO compound, the additional band that can be seen from around 2 eV to 3.5 eV is contributed by the Mg-3s empty states. It is clearly seen that the distance between the empty and filled Co-3d states in the NMCO compound is shorter than in the NCO compound.

The Seebeck coefficient that was calculated using BoltzTrap program and plotted against temperature is shown in figure 5. We plotted the Seebeck coefficients of NCO and NMCO compounds with $x = 0.375$ and 0.875. Seebeck coefficients from all compounds increase and temperature increases. For low Na concentration Seebeck coefficient is lower than for high Na concentration. It could be seen also that for NCO compound, the calculation predict the positive sign of Seebeck coefficient. Meanwhile, for the substitution of Mg$^{2+}$ will change the sign of Seebeck coefficient at low temperature below 100 K. For the high temperature there are no significant differences between the NCO and the NMCO compound, therefore, the Mg$^{2+}$ substitution will not change the Seebeck coefficient at high temperature.
Figure 5. Plot of calculated Seebeck coefficient against temperature for NCO and NCMO compound with Na concentration of 0.375 and 0.875.

4. Summary

First principle calculations have performed on the Na$_x$CoO$_2$ and (Na, Mg)$_x$CoO$_2$. The lattice parameters of those compounds depend on the Na concentration. The substitution of Mg$^{2+}$ ions at the Na sites will reduce the lattice parameter $c$ but enlarge the lattice parameter $a$. The calculated enthalpy of formation of NCO indicates the presence of two stability region separated at $x = 0.55$ and the Mg$^{2+}$ substitution would increase the stability of NCO compound. The Mg$^{2+}$ slightly affects the band structure especially to the electronic structure of Co-3$d$ states and the conduction band. The calculated Seebeck coefficient predicted that the Mg$^{2+}$ substitution would not affect the Seebeck coefficient at high temperature.

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