First Principles Study of $NaMnNbPO_4$ as a Cathode Material for Sodium-Ion Battery

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Abstract. Sodium ion batteries (SIBs) are emerging as a sustainable and cost-effective alternative to lithium-ion batteries due to the natural abundance and low cost of sodium. This study employs first-principles density functional theory (DFT) to explore the structural, electronic, mechanical, and thermal properties of $NaMnPO_4$ and its niobium-doped variant, $NaMnNbPO_4$, as cathode materials for SIBs. The results show that Nb doping causes a slight increase in lattice parameters and volume, indicating minimal structural distortion. Electronic density of states (DOS) analysis revealed that $NaMnPO_4$ is a semiconductor, while Nb doping induces a transition toward half-metallic behaviour. The doped compound also exhibits enhanced mechanical rigidity and improved thermal stability, evidenced by higher elastic moduli, sound velocities, and Debye temperature. These improvements suggest that Nb-doped $NaMnPO_4$ is a promising high-performance cathode material for next-generation sodium-ion batteries.

1. Introduction

The increasing demand for sustainable energy solutions, such as solar, wind and tidal power has led to the advancement of electrochemical energy storage (EES) systems. EES is a clean and environmentally friendly technology that converts electric energy and chemical energy into energy storage and releases it through chemical reactions [1]. Among the various EES technologies, rechargeable batteries play a vital role in producing clean energy storage because they are cost-effective, require low maintenance, and have a long cycle life. Lithium-ion batteries (LiBs) are widely used as an energy storage system in portable devices (e.g., laptops, tablets and phones) particularly due to their high energy density and extended lifespan. However, the limited amount of lithium on Earth has led to high manufacturing costs, causing a hindrance to its application in large-scale energy storage systems. Thus, there is an urgent need for an alternative to lithium-based batteries. Sodium and lithium both share similar physical and chemical characteristics as they are members of the same group in the periodic table, the alkali-metals [2]. Sodium is the sixth richest element in the Earth's crust and is widely available in the

form of sodium chloride (common salt) [3], which further reduces production costs. Hence, sodium-ion batteries have gained significant attention as a promising alternative for LiBs.

Despite sharing similar intrinsic properties to those of LiBs, the larger ionic radius and high atomic weight of sodium leads to sluggish ionic movement between the electrodes and increases the stress on the host material during cycling, which can result in lower energy density and shorter cycle lifetime [4-6]. Consequently, there is a need to identify and enhance electrode materials with better electrochemical performance including high energy density, and longer lifespan. In recent years, several studies have been conducted on improving cathode materials, as it directly affects cycle performance and further reduces the overall energy density that can be achieved. Among various cathode materials (transition metal oxides, polyanionic compounds, Prussian blue and other organic compounds) [2], transition metal phosphates, $NaMP0_4$ (M = Ni, Co, and Mn) is considered a suitable cathode material for sodium-ion batteries due to high thermal stability and high cut-off voltages [7-9]. A study done by Dima et al. [10] investigated the stability and the voltage window of $NaMnP0_4$ using first principle calculations that were focused on density functional theory (DFT). The lattice parameter and cell volume changes were found to be less than 7 %, indicating that the structure remained intact during the discharging process[REF]. The voltage value was found between 5.132 V and 4.655 V, which implied that the voltage window is suitable to be applied as SiBs cathodes, and $NaMnP0_4$ could be treated as a potential SiB cathode material. In this study, DFT was used to investigate the electrochemical performance of $NaMnPO_4$, focusing on its structural, electronic, and thermal properties. To enhance its electrochemical performance and electronic conductivity, Nb substitution was introduced to form $NaNbMnPO_4$, with the aim of developing a high-voltage cathode material suitable for next-generation sodium-ion batteries (SIBs).

2. Computational method

Density functional theory (DFT) calculations were performed using the Vienna Ab Initio Simulation Package (VASP) code. A spin-polarised generalised gradient approximation (GGA) was used to solve the Kohn-Sham equations with the Perdew-Burke-Ernzerhof functional (PBE) exchange-correlation functional with plane-wave pseudopotential. Geometry optimisation for the ground state energy of $NaMnPO_4$ was performed. The plane wave cutoff energy of 560 eV and the Monkhorst-Pack scheme were used with a 5 x 5 x 7 k-point mesh. The random substitution doping technique was used to introduce Nb atoms into $NaMnPO_4$ followed by calculating the structural, mechanical, electronic and thermodynamic properties of the bulk structure of $NaMnPO_4$ and $NaMnNbPO_4$.

3. Results and discussion

3.1. Structural properties

The structural properties of NaMnPO4 and NaMnNbPO4 have been calculated and are presented in Table 1. The structural properties for NaMnPO4 have been calculated and are compared with previous DFT and experimental literature values. The computed values for $NaMnPO_4$ align closely with those obtained from experimental results and other prior DFT studies [10]. The substitution of Mn with Nb results in a slight increase in the lattice parameter and unit cell volume, suggesting that Nb doping leads to minimal structural distortion. The lattice parameter a exhibited a decrease, whereas b and c showed a slight increase.

Table 1: Structural Properties of NaMnPO4 and $NaMnNbPO_4$

	Literature		$NaMnPO_4$	Deviation		$NaMnNbPO_4$
	Experimental [10]	DFT [10]		Experimental	DFT	
a(Å)	10.528	10.421	9.093	9.093	1,435	4.923
b(Å)	6.321	6.132	6.864	6.864	0.188	6.449
c(Å)	4.985	4.864	5.091	5.091	0.106	10.195
Volume ($Å^3$)	331.740	310.579	322.101	322.101	9.639	323.149
Band gap (eV)		3.161	3.161	3.370		0.185

The unit cell volume of $NaMnPO_4$ increased from 310.579 $Å^3$ to 322.101 $Å^3$ in the doped structure, suggesting successful incorporation of the Nb atom without compromising the structural stability of the host material [4]. These changes are attributed to the larger atomic radius of Nb compared to Mn, which results in a small lattice expansion. Despite this expansion, the overall orthorhombic crystal structure remains intact, demonstrating that $NaMnPO_4$ can accommodate Nb substitution without significant degradation [4].

3.2. Electronic properties

The electronic properties of $NaMnPO_4$ and $NaMnNbPO_4$ were examined through an analysis of their spin-polarised density of states (DOS). This enhanced the comprehension of the material's electron behaviour and its capacity to conduct electricity.

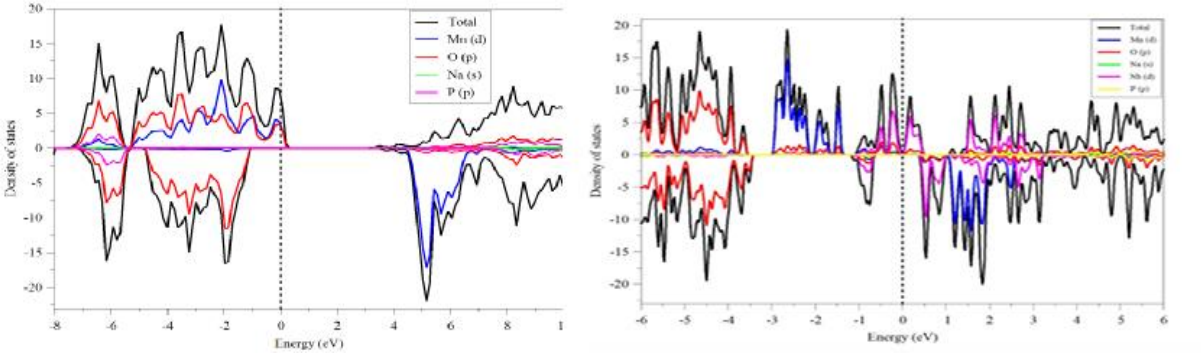

Figure 1. Spin Polarised DOS of NaMnPO4 and NaNbMnPO4

The density of states for $NaMnPO_4$ indicates a distinct energy gap separating the valence band from the conduction band. This indicates that it functions similarly to a semiconductor, requiring a certain amount of energy to facilitate electron movement and enable current flow. This property is advantageous for battery materials, as it regulates electron movement during charging and discharging [4]. After doping with niobium (Nb), the DOS of $NaMnNbPO_4$ changed. The energy gap became smaller in one of the spin channels, and part of the gap disappears. This indicates that the material is now partly metallic in one spin direction, while still semiconducting in the other. This behaviour is known as half-metallic and hence can be advantageous in batteries as they enhances electrical conductivity while maintaining regulation of electron flow. The enhanced conductivity in $NaMnNbPO_4$ may augment the efficiency of sodium-ion batteries by facilitating electron mobility within the material during operation.

3.3. Mechanical properties

The mechanical properties of $NaMnPO_4$ and $NaMnNbPO_4$ were studied using their elastic constants. These values allow us to determine how strong and stable the materials are under pressure or stress.

$$(C_{11} + C_{12}), (C_{11} + C_{33} + 2C_{13}) > 0$$

$$(2C_{11} + C_{33} + 2C_{12} + 4C_{13}) > 0$$
$$C_{11} > 0, C_{33} > 0, C_{44} > 0 \; and \; C_{44} > 0$$

Table 2: Elastic constants (Cij) for $NaMnPO_4$ and $NaMnNbPO_4$

	$NaMnPO_4$	**$NaMnNbPO_4$**
C_{11}	124.46	172.12
C_{12}	61.43	52.22
C_{13}	58.55	79.79
C_{22}	125.29	200.71
C_{23}	51.49	60.73
C_{33}	148.46	148.49
C_{44}	42.28	59.36
C_{55}	49.01	58.47
C_{66}	46.71	58.41

The findings demonstrate that all elastic constants are positive and meet the mechanical stability criteria for orthorhombic crystals. This suggests that both materials demonstrate mechanical stability, an essential aspect for materials employed in battery applications. Comparing the two materials reveals that $NaMnNbPO_4$ demonstrates higher values for most elastic constants. This suggests that incorporating Nb improves the material's strength and stiffness.

Table 3: Bulk, shear and Young's moduli, Poisson's and Pugh's ratio

	B_H	G_H	E_H	B/G	V
$NaMnPO_4$	81.48	42.36	108.30	1.924	0.275
$NaMnNbPO_4$	99.42	55.36	141.15	1.780	0.263

After doping $NaMnPO_4$ with Nb, a notable enhancement in mechanical strength was recorded. The bulk modulus (B), which reflects the resistance to volume change under pressure, increased from 81.48 in the undoped compound to 99.42 in the doped structure. Similarly, the shear modulus (G), which pertains to the resistance against shape deformation, increased from 42.36 to 55.86. The Young's modulus (E), a measure of overall stiffness, increased from 108.30 to 141.15. The observed increases indicate that Nb doping enhances the material's strength and improves its resistance to mechanical deformation.

The analysis focused on Pugh's ratio (B/G) and Poisson's ratio (v) to assess the ductility of the materials. A Pugh's ratio exceeding 1.75 typically signifies ductile behaviour. The values for $NaMnPO_4$ and $NaMnNbPO_4$ were found to be 1.924 and 1.780, respectively, indicating that both materials exhibit ductility. The values of Poisson's ratio were determined to be 0.278 for $NaMnPO_4$ and 0.263 for $NaMnNbPO_4$. The value exceeds 0.25, indicating that the material exhibits ductilit

The results indicate that Nb doping preserves the structural integrity of $NaMnPO_4$ while simultaneously improving its mechanical strength and flexibility. Consequently, $NaMnNbPO_4$ demonstrates enhanced durability and dependability as a cathode material in sodium-ion batteries [2].

3.4. Thermodynamic properties

The Debye temperature (θ_D) was calculated from the average sound velocity (v_m) using the equation [10]:

$$\theta_D = \frac{h}{k_B}\left(\frac{3}{4\pi}\right)^{\frac{1}{3}} v_m \quad (1)$$

where h and k_B are Planck's and Boltzmann's constants, respectively, the average sound velocity in polycrystalline systems, v_m, is evaluated by the expression:

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{-\frac{1}{3}} \quad (2)$$

where v_t and v_l are the mean longitudinal and transverse sound velocities, which can be related by the shear and bulk moduli from Navier's equations:

$$v_t = \left(\frac{3B+4G}{3\rho}\right)^{\frac{1}{2}} \quad (3)$$

$$v_l = \left(\frac{G}{\rho}\right)^{\frac{1}{2}} \quad (4)$$

Table 4: Calculated volumetric density, sound velocities, and Debye temperature

	p	V_t	V_i	V_m	θ_D
$NaMnPO_4$	3309	3576	6634	3984	512.7
$NaMnNbPO_4$	3944	3760	6454	4181	551.1

With the introduction of the Nb dopant, there was an observed increase in both the average sound velocity and the Debye temperature. The Debye temperature increased from 512.7 K for $NaMnPO_4$ to 551.1 K for $NaMnNbPO_4$. This increase suggests that Nb-doped $NaMnPO_4$ exhibits enhanced bonding and improved thermal stability. The observed enhancements indicate that the doped material exhibits superior capabilities in managing heat and mechanical vibrations, thereby rendering it more appropriate for prolonged application in sodium-ion batteries.

4. Conclusion

The density functional theory was employed to explore the impacts of Nb doping on the structural, electronic, mechanical, and thermal characteristics of $NaMnPO_4$. The findings indicate that the doped material maintains structural stability with negligible distortion. Nb substitution resulted in alterations to the electronic structure, indicating a decrease in the band gap and evidence of half-metallic behaviour, which could enhance electrical conductivity. Furthermore, the doped compound demonstrated improved mechanical strength and thermal stability, as evidenced by elevated elastic moduli and Debye temperature. The integration of these enhancements' positions $NaMnNbPO_4$ as a highly promising candidate for sodium-ion battery cathodes with superior performance.

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References

1. Yang, H., Zhang, S., Chen, B., Xiang, S., Xu, Y., Yin, B., & Ackom, E. (2023). The battery storage management and its control strategies for power system with photovoltaic generation. In *Emerging Trends in Energy Storage Systems and Industrial Applications* (pp. 441-484). Academic Press.
2. M. He, S. Liu, J. Wu, and J. Zhu, "Review of cathode materials for sodium-ion batteries," *Progress in Solid State Chemistry*, vol. 74, pp.100452, 2024, doi: https://doi.org/10.1016/j.progsolidstchem.2024.100452.
3. P. Phogat, S. Dey, M. Wan, "Comprehensive review of sodium-ion batteries: Principles, materials, performance, challenges, and future perspectives, " *Materials Science and Engineering: B*, vol. 312, pp. 117870, 2025, doi: https://doi.org/10.1016/j.mseb.2024.117870.
4. G. Li, X. Lou, C. Peng, C. Liu, and W. Chen, "Interface chemistry for sodium metal anodes/batteries: a review". *Chemical Synthesis*, vol. 2, no. 3, 2022, doi: https://doi.org/10.20517/cs.2022.19.

5. A. Rudola, K. Saravanan, S. Devaraj, H. Gong, and P. Balaya, "Na 2 Ti 6 O 13: a potential anode for grid-storage sodium-ion batteries, " *Chemical Communications*, vol. 49, no. 67, pp.7451-7453, 2013, doi: https://doi.org/10.1039/C3CC44381G.
6. H.W Kim, H. J. Kim, H. Byeon, J. Kim, J.W. Yang, Y. Kim, and J.K. Kim, "Binder-free organic cathode based on nitroxide radical polymer-functionalized carbon nanotubes and gel polymer electrolyte for high-performance sodium organic polymer batteries, " *Journal of Materials Chemistry A*, vol. 8, no.35, pp.17980-17986, 2020, doi: https://doi.org/10.1039/D0TA04526H.
7. M. Minakshi, D. Mitchell, R. Jones, F. Alenazey, T. Watcharatharapong, S. Chakraborty, R. Ahuja, "Synthesis, structural and electrochemical properties of sodium nickel phosphate for energy storage devices," *Nanoscale*, vol. 8, no. 22, pp.11291-11305, 2016, doi: https://doi.org/10.1039/C6NR01179A.
8. M. Minakshi, D. Meyrick, "Reversible sodiation in maricite NaMn1/3Co1/3Ni1/3PO4 for renewable energy storage, " *Journal of alloys and compounds,* vol. 555, pp.10-15, 2013, doi: https://doi.org/10.1016/j.jallcom.2012.11.203.
9. K.T. Lee, T.N. Ramesh, F. Nan, G. Botton, L.F. Nazar, "Topochemical synthesis of sodium metal phosphate olivines for sodium-ion batteries." *Chemistry of Materials*, vol. 23, no.16, pp.3593–3600, 2011, doi: https://doi.org/10.1021/cm200450y.
10. R.S Dima, P.M. Maleka, E.N. Maluta, R.R. Maphanga, "First principles study on sodium de-intercalation from NaMnPO4." *Materials Today: Proceedings,* vol. 62, pp. S7-S11, 2022, doi: https://doi.org/10.1016/j.matpr.2022.02.076.