RESEARCH ARTICLE

FIRST-PRINCIPLES STUDY OF OLIVINE-TYPE NAMNPO$_4$ AS POSITIVE ELECTRODE MATERIALS FOR RECHARGEABLE SODIUM ION BATTERIES.

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Manuscript Info	*Abstract*
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The diffusion mechanism of Na ions in the olivine-type NaMnPO$_4$ is investigated by first-principles calculations. Electron transport properties studied by first-principles density functional theory (DFT) GGA+U method and achieved Final Energy/Atom -7.03 eV. The calculated diffusion energy was 0.65 eV for Na to diffuse along the (0 1 0) direction. The large inter and intra-layer distance of Mn 3.156 A^o and 6.312 A^o offers feasible channels for fast Na ion diffusion in (0 1 0) direction. Implications of first-principles calculations useful strategy for better understanding the electrochemical properties of olivine-type NaMnPO$_4$ are discussed for designing better-performing Na ion rechargeable batteries.

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Introduction:-
Sodium-ion batteries have vast potential as an inexpensive, geopolitically-neutral alternative to Li-based rechargeable batteries, largely due to the global abundance and low cost of sodium-containing precursor materials. Na-ion electrode materials, while conceptually similar to their Li-ion counterparts, give rise to unique challenges and physical properties due to sodium's larger size and lower absolute standard electrode potential. Due to their larger size, Na ions can reversibly intercalate in more materials than Li-ions, giving a much broader chemical space in which electrode materials can be optimized. This, together with sodium's abundance, makes Na-ion batteries excellent candidates for large-scale energy storage [1-4]. In this computational studies with the goal of novel Na-ion electrode discovery, as well as material optimization and understanding of the underlying physics governing material function. First-principle computational efforts are used to obtain insights into phase transitions during electrochemical deintercalation of Na-ion cathodes, as well as diffusion mechanics and diffusivity. High throughput computation is utilized to search for the novel cathode, anode, and solid electrolyte materials. In this paper, we examine olivine-type NaMnPO$_4$ using first-principles calculations. It has been noted that LDA and GGA give relatively large errors for the sodium intercalation potentials. So we purpose is to extend such calculations to other compounds of the phospho-olivine family and to show that treating electronic correlations within the GGA+U method gives considerably better agreement with experiment and thereby provides a tool to accurately predict Na intercalation potentials. We first present the details of the GGA+U method as well as structural information on the Sodium-orthophosphate oxides and show how the electrochemical reactions take place in a rechargeable Sodium ion battery.

Computational methods:-
The First principle calculations have been performed using the Quantum ESPRESSO PWscf code [5] using a plane-wave basis to express the wave function of the valence electrons and ultrasoft pseudopotentials to describe the

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interactions of ionic cores and valence electrons [6]. QuantumWise VNL-ATK 2016 academic version was used as GUI for Quantum ESPRESSO. The exchange-correlation contribution was described by the generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof [7]. Onsite Coulomb correction (GGA + U) was included to describe the localized electronic states of Mn 3d in mixed-valence rare earth metals. A spin polarization calculation was used. A kinetic cutoff energy of 520 eV, and $5 \times 5 \times 3$ k-point meshes in the $NaMnPO_4$ unit cell (28 atoms) were found by a convergence test (<3 meV/$NaMnPO_4$). Because the band gaps of both compounds were underestimated, which is typical of the GGA + U functional [8]. The relaxation of unit cell volume was done by total energy minimization, and atom positions were relaxed until the remaining force acting on the atoms was less than 10^{-3} eV/Å. The Na diffusion in $NaMnPO_4$ is calculated by Na jumps between neighboring M1 sites were obtained by means of the nudged elastic band (NEB) method [9]. The threshold for the total force that is acting on the NEB images of the interpolated reaction path was set to 0.05 eV/Å.

Results and discussion:-

Figure 1. Shows the bulk crystal structure of sodium Manganese phosphate [$NaMnPO_4$] with orthorhombic (ICSD - 201771) with space group Pnma. The olivine structure of the $NaMnPO_4$ is a hexagonal close-packed array of oxide ions containing isolated PO_4 tetrahedral and corner-sharing MnO_6 octahedra in the (0 1 1) plane and edge-sharing NaO_6 octahedral, stacked along the [0 1 0] direction. Because the oxygen atoms are strongly bonded to both Mn and P atoms.
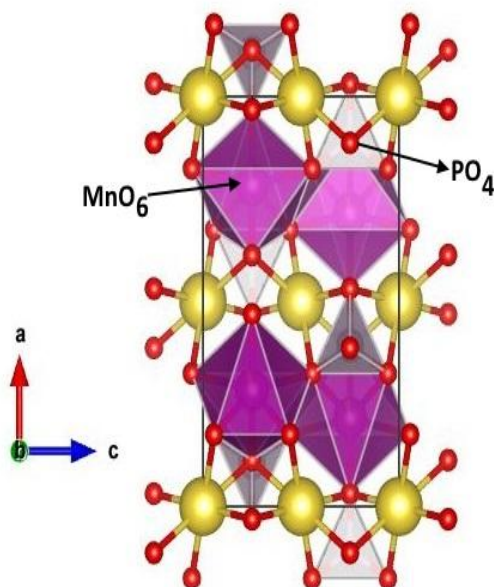

Figure 1:- Crystallographic structure of the bulk $NaMnPO_4$ (Yellow, red, gray and purple balls refer to Na, O, P and Mn atoms, respectively).

The optimized lattice constants for the $NaMnPO_4$ are summarized in Table 1, along with other experimental values. The calculated values are larger than the experimental ones, but the errors of the computed values compared with the experimental ones are within 0.04–0.33%. The underestimation of the lattice constant compared with the equilibrium values is due to the feature of GGA functional used.

Table 1:- Optimized lattice constants for olivine-type $NaMnPO_4$ (Å)

		a Å	b Å	c Å	reference
$NaMnPO_4$	Exp.*	5.155	6.976	9.210	ICSD ID 201771
	Computed	5.172	6.981	9.214	This work

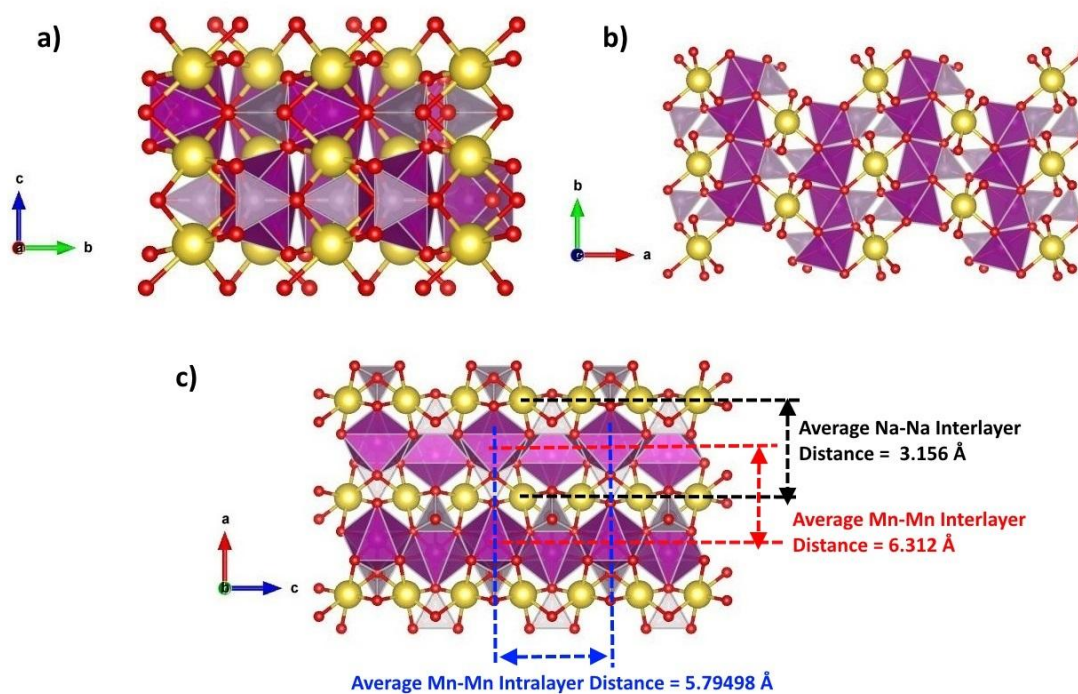*** J. Moring and E. Kostiner, J. Solid State Chem., 1986, 61, 379–383.**

Figure 2:- Crystallographic structures of NaMnPO$_4$ a) 100 b) 001 c) 010 directions

Figure 2. shows structural illustration of olivine-type NaMnPO$_4$ (100), (001), (010) directions and Figurer 2c shows the Na-diffusion channels in NaMnPO4 in (010) directions. It offers more interlayer Mn–Mn distance (6.312 A°) than the inter-layer Mn-Mn distance (5.794 A°), which facilitates two-dimensional Na-ion diffusion pathways to achieve the fast intercalation and de-intercalation phenomena along the a and c directions. These free wider paths offer fast Na ion in NaMnPO$_4$.
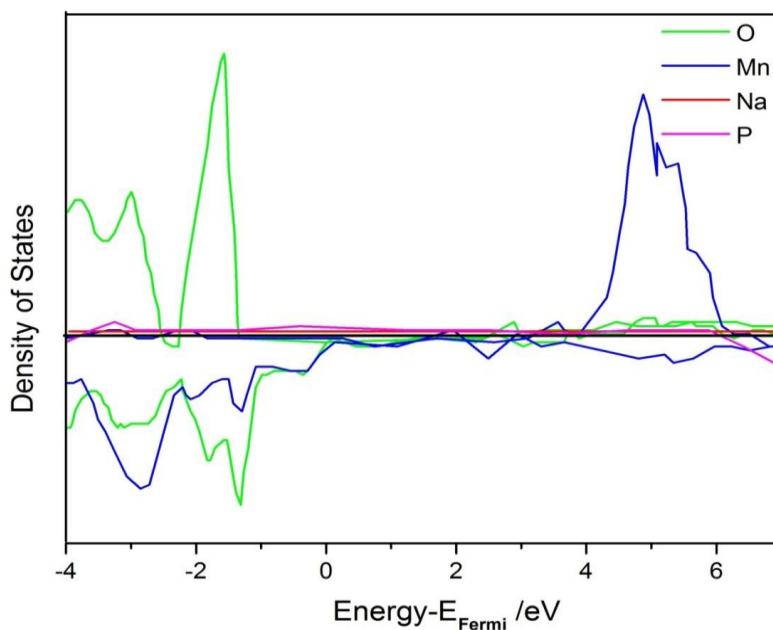

Figure 3:- Partial density of states (PDOS) for NaMnPO$_4$ (PDOS is aligned so that the Fermi energy is zero)

Figure 3. shows the partial density of states (PDOS) around the Fermi level for olivine-type NaMnPO$_4$, respectively. The localized Mn 3d bands form a valence band maximum and conduction band minimum, and the band gaps are larger than 3.051 eV in NaMnPO$_4$. Therefore, the intrinsic band conduction of electrons is negligible at room temperature because of the localization and wide band gap. Electronic conduction in NaMnPO$_4$ mainly arises from localized electron/hole (polaron) hopping. [10] Polarons are created by the redox reaction of Mn$^{2+/3+}$ to maintain charge neutrality during electrochemical Na$^+$ removal (uptake). In Figure. 3 the calculated energy profiles for localized hole (Mn^{3+}) jumps of ~0.2 eV for both compounds. The polaron migration energies are much smaller than the band gaps, and thus polaron migration is the dominant electron conduction mechanism. The similarity of the polaron migration energies of the two compounds indicates that the difference in rate performance does not stem from polaronic migration. Alkali ion migration is another factor affecting the rate performance in batteries.
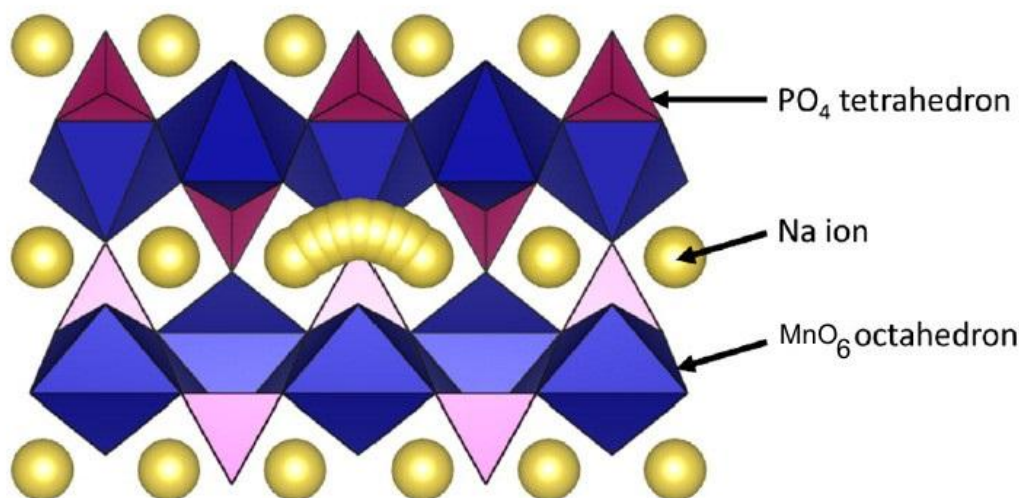

Figure 4:- Trajectory of Na ions in the NaMnPO$_4$ bulk structure calculated by the NEB method.

NEB calculations were performed to evaluate the migration energies of alkali ions NaMnPO$_4$. The GGA functional was used to avoid the effect of complicated polaron interactions. Figure 4 shows the migration trajectory of Na+ hopping in the NaMnPO$_4$ bulk structure. Na ions at the octahedral site jump to the neighboring site via the tetrahedral vacancy site along the (0 1 0) direction, forming a one-dimensional pathway. The migration energy profiles are shown in Figure 5, where the energy maximum is located at the center of migration path (tetrahedral vacancy).
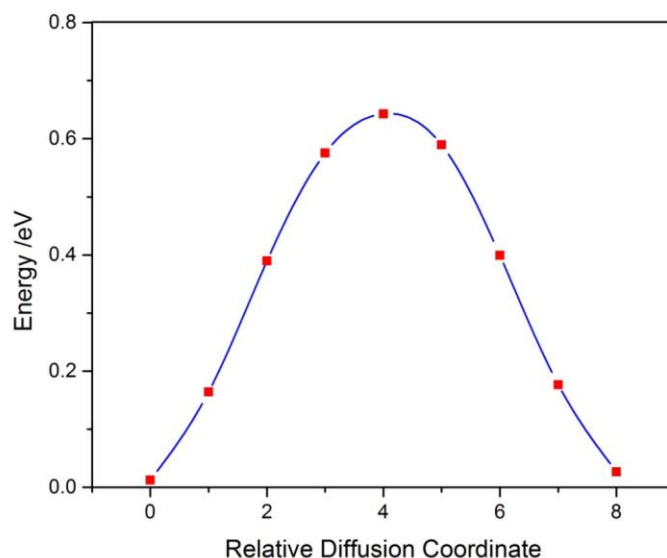

Figure 5:- Diffusion energy curves of Na in bulk NaMnPO4

The migration energy 0.65 eV achieved in NaFePO4. The migration energy 0.65 eV is quite higher than in $LiMnPO_4$ because Na^+ is slightly larger than that of Li^+, which may arise from the size effect of the larger ionic radius of 6-coordinate Na+ (1.02 Å) compared with Li+ (0.76 Å). the diffusion coefficient, D, can be expressed by migration energy, Em, as follows,

$$D = a^2\, v^* \exp\left(\frac{-E_m}{K_B T}\right) \ldots\ldots (1)$$

Where a, v^*, k_B and T correspond to hopping distance, attempt frequency, Boltzmann constant, and absolute temperature, respectively.

Interfacial migration mechanism (Figure 6) indicate that a fast charge–discharge mechanism occurs in $Na_{1-x}MnPO_4$ electrodes owing to the interfacial Na ion migration mechanism (Em ~ 0.15 eV) as proposed in the domino-cascade model, whereas a bulk conductivity mechanism is dominant in the $Na_{1-x}MnPO_4$ electrode (Em ~ 0.65 eV) because of the miscibility in terms of Na/vacancy arrangements in the lattice.
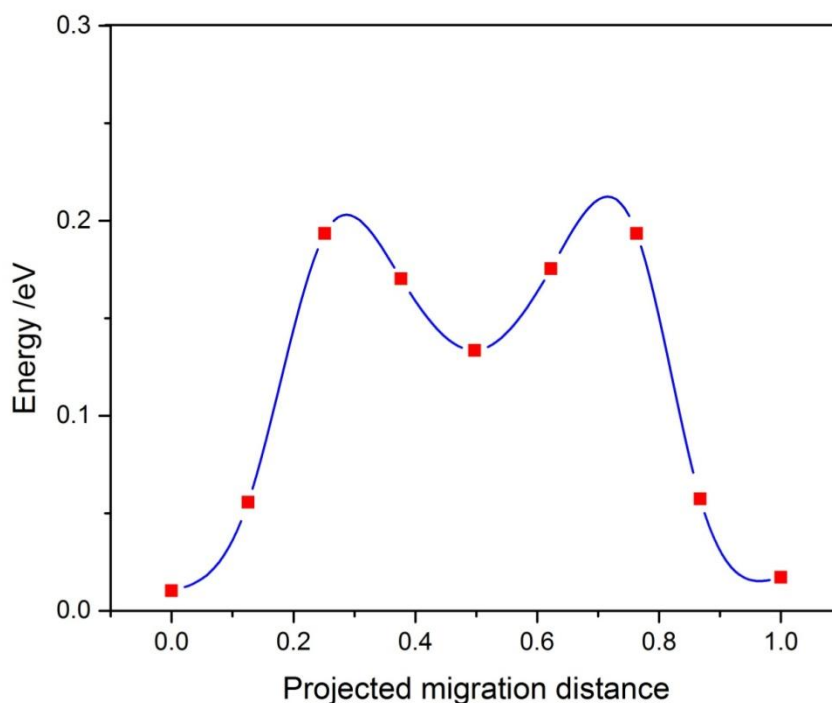

Figure 6:- Calculated migration energy of alkali ions at the (010) interface for $NaMnPO_4$/ $MnPO_4$

In addition, a phase transition will occur during the charge and discharge processes in $NaMnPO_4$ electrode material, thus a correction to the method will be required to calculate the voltages for Sodiation/deSodiation caused by the phase transition. Moreover, the energy of Sodiation/desodiation is very small in some electrode materials, much smaller than the activation energy of Na migration.

Conclusion:-
First Principle calculation of olivine-type $NaMnPO_4$ successfully studied by Density function theory. The calculated diffusion energy barriers of the bulk $NaMnPO_4$ and 0.65 eV. We Studied bulk polaron migration mechanism (Figure 5), and bulk alkali ion migration mechanism (Figure 6). Therefore, the difference in alkali ion size is not a major factor controlling the rate performance of the charge–discharge reaction. However, the phase stability of olivine-type compounds indicates a two-phase reaction mechanism for the $NaMnPO_4$ electrode Our results suggest that faster Na^+ migration at the interface than in the bulk originates from the two-phase reaction mechanism. Accordingly, the formation of the interface in $NaMnPO_4$ may play an important role in the fast charge– discharge properties of olivine-type electrodes.

References:-

1. Palomares, Verónica, et al. "Na-ion batteries, recent advances and present challenges to become low cost energy storage systems." *Energy & Environmental Science* 5.3 (2012): 5884-5901.
2. Slater, Michael D., et al. "Sodium-ion batteries." *Advanced Functional Materials* 23.8 (2013): 947-958.
3. Pan, Huilin, Yong-Sheng Hu, and Liquan Chen. "Room-temperature stationary sodium-ion batteries for large-scale electric energy storage." *Energy & Environmental Science* 6.8 (2013): 2338-2360.
4. ''Basic research needs for electric energy storage'' (United State Department of Energy, 2007).
5. Giannozzi, Paolo, et al. "QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials." *Journal of physics: Condensed matter* 21.39 (2009): 395502.
6. Vanderbilt, David. "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism." *Physical Review B* 41.11 (1990): 7892.
7. Perdew, John P., Kieron Burke, and Matthias Ernzerhof. "Generalized gradient approximation made simple." *Physical review letters* 77.18 (1996): 3865.
8. Da Silva, Juarez LF, et al. "Publisher's Note: Hybrid functionals applied to rare-earth oxides: The example of ceria [Phys. Rev. B 75, 045121 (2007)]." *Physical Review B* 75.8 (2007): 089901.
9. Islam, M. Saiful, and Craig AJ Fisher. "Lithium and sodium battery cathode materials: computational insights into voltage, diffusion and nanostructural properties." *Chemical Society Reviews* 43.1 (2014): 185-204.
10. Ong, Shyue Ping, et al. "Voltage, stability and diffusion barrier differences between sodium-ion and lithium-ion intercalation materials." *Energy & Environmental Science* 4.9 (2011): 3680-3688.