Size Induced Structural Changes in *maricite*-$NaFePO_4$: An In-Depth Study by Experimental and Simulations†

Monika Sharma,[1] Mukul Gupta,[2] Payam Kaghazchi[3,4] and Sevi Murugavel[1*]

[1]*Department of Physics and Astrophysics, University of Delhi, Delhi–110 007, India*
[2]*UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore - 452 001, India*
[3]*Physikalische und Theoretische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Takustraße 3, 14195 Berlin, Germany*
[4]*Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research (IEK-1), Materials Synthesis and Processing, Wilhelm-Johnen-Straße, 52425 Jülich, Germany*

ABSTRACT: Rechargeable batteries based on the most abundant elements such as sodium and iron has a great potential in developing cost effective sodium ion batteries for large scale energy storage devices. We report, for the first time, crystallite size dependent structural investigations on *maricite*-$NaFePO_4$ through x-ray diffraction, x-ray absorption spectroscopy and theoretical simulations. Rietveld refinement analysis on the x-ray diffraction data reveals that decrease in the unit cell parameters which lead to the volume contraction upon reduction in the crystallite size. Further, the atomic multiplet simulations on x-ray absorption spectra provide unequivocally the change in the site symmetry of transition metal ion. The high resolution oxygen K-edge spectra reveal substantial change in the bonding character with reduction of crystallite size, which is the fundamental cause for the change in unit cell parameters of *maricite*- $NaFePO_4$. In parallel, we performed first-principles density functional theory (DFT) calculations on *maricite*-$NaFePO_4$ with different sodium ion vacancy concentrations. The obtained structural parameters are in excellent agreement with the experimental observations on the mesostructured *maricite*-$NaFePO_4$. The volumetric changes with respect to crystallite size are related to the compressive strain resulting into the improvement in the electronic diffusivity. The nano-crystalline *maricite*-

$NaFePO_4$ with better kinetics will open the new avenue for its usage as cathode material in sodium ion batteries.

†Electronic supplementary information (ESI) available

Introduction

The development of new and novel electrode materials for energy storage devices has become an intensive research by the materials science community because of its importance in the portable electronic devices, electrical vehicles and many other applications [1, 2]. During the last two decades lithium ion batteries have been ruling the world with their better electrochemical performance as well as the advancement in the newer technology which is based on the new electrode and electrolyte materials. The development of lithium ion battery includes the discovery of many new electrode materials along with the modifications in the existing electrode and electrolyte materials [3-5]. As per the global demands for the requirement of energy storage/supply increasing exponentially, the prices of the lithium ion batteries are also rising day by day due to limited resources of lithium in the earth-crust [6]. In such situations, we need to address with the low cost and high natural abundant element-based batteries. In this regard, the fifth most abundant material in the earth-crust and second lightest element among the alkali metals is sodium. Hence, sodium-based cathode material could be the alternative choice for the next generation of rechargeable batteries [7, 8]. The olivine structured polyanionic compounds $LiMPO_4$ (M= Fe, Mn, Ni, and Co) have emerged as a promising class of cathode material for lithium ion batteries [9-11]. More specifically, the $LiFePO_4$ (LFP) became much of interest due to its attractive electrochemical performance (high operating voltage and large gravimetric capacity), low cost and good chemical stability during lithiation-delithiation [12, 13]. Based on the good performance characteristics, LFP has already found widespread application in battery industries [14]. In order to develop low-cost and large-scale rechargeable batteries, the scientific research community as well as commercial industries try to adopt chemical equivalent of olivine-type $NaFePO_4$ (NFP) as cathode material by expecting similar electrochemical properties of LFP. Unlike LFP, NFP crystallizes in two structures namely *triphylite* and *maricite* belongs to the orthorhombic phase [15]. However, it has been found that the olivine-type NFP is not thermodynamically stable phase, and the routine solid-state synthesis results the formation of *maricite* NFP (m-NFP). An important difference between *triphylite* and *maricite* is the site occupancy of alkali and transition metal ions. In *maricite* structure, the Na^+ ion occupies the M2 site, and transition metal ion (here Fe^{2+}) occupies the M1 sites, where edge-shared FeO_6 octahedrons form one-dimensional chains along the *b*-axis, and these chains are linked by PO_4 tetrahedra to form 3D structure. Thus, there are no cation channels for the fast alkali ion diffusion, contrary to the *triphylite* LFP.

Interestingly, the NFP possess relatively high theoretical capacity of 155 $mAhg^{-1}$ in comparison with the other iron-based cathode materials for the sodium ion batteries [16-18]. The olivine NFP can be prepared only via electrochemical ion exchange process, i.e. exchange of Li ions in LFP with Na^+ ions. Further, the sodiation of $FePO_4$ structure delivers a practical reversible capacity of 120 $mAhg^{-1}$ [19]. On the other hand, all the chemical and mechano-chemical process adopted for synthesis results into the thermodynamically stable *m*-NFP structure. It has been believed that in m-NFP, due to lack of one-dimensional channels for alkali ion transport, it is of less interest as cathode material for battery applications. However, a recent report on the m-NFP structure reveals that smaller particle sized m-NFP found to exhibit superior electrochemical performance and suggested as possible cathode material for the sodium ion batteries [20]. In general, the slower kinetics of cathode materials and in particular m-NFP may be influenced by diffusion-controlled resistance, namely, the electron and ion transport properties. Importantly, the ionic radius of Na^+ is larger than the Li^+, which could increase the migration energy for diffusion. In addition, the earlier studies also revealed that the diffusion coefficient of Na^+ is significantly lower than that of Li^+ in olivine type orthophosphate structure [21, 22].

In this work, we demonstrate the feasibility of crystallite size effect on the structural properties of m-NFP, which would ultimately lead to higher electrode/electrolyte contact area, reduced diffusion path length of polarons/sodium ions and an enhanced reaction rate. In this direction, we have synthesised single phase m-NFP by the solid-state route with different crystallite sizes starting from bulk (80 nm) to 25 nm. With the help of various analytical techniques, we have confirmed single phase formation in all the crystallize sizes with no other parasitic phase contribution in the structure. More importantly, the structural analysis carried out with x-ray diffraction data combined with Rietveld refinement method provides systematic changes in the unit cell parameters with varying the crystallite size. The observed systematic changes in structural behaviour of m-NFP with crystallite size are closely linked with the modifications in the hybridization between transition metal ion and ligand orbital revealed by x-ray absorption spectroscopy (XAS) technique. In parallel with experimental work, we have applied density functional theory (DFT) with generalized gradient approximation (GGA) and Hubbard term (U) calculation with different super cell sizes to reveal the corresponding structural properties of m-NFP. The obtained DFT results are in agreement with the experimental data. We suggest that the observed structural variations with crystallite size would have strong impact on the electronic properties of mesostructured m-NFP, which ultimately could open door for the electrochemically inactive m-NFP as promising cathode material for advanced sodium ion batteries.

Methods

Synthesis of *maricite* $NaFePO_4$ (NFP)

Maricite NFP with different crystallite sizes has been prepared by using the solid-state route. The precursors used for the synthesis were high purity Na_2CO_3 (99.95%), $FeC_2O_4.2H_2O$ (99.99%) and $NH_4H_2PO_4$ (99.999%) in stoichiometric ratio mixed together and ground to homogenize the mixture. Afterwards, the mixture was then transferred to the alumina boat and fired at 750 °C in the reducing atmosphere (90% N_2 +10% H_2), which results the bulk m-NFP sample with the 80 nm crystallite size. In order to synthesize the lower crystallite sized particles, we have varied the synthesis temperature along with the process timings Table TS1 (ESI). An obtained powdered sample was then ground and moulded into various shapes for further characterizations. The details of the experimental conditions used for obtaining different crystallite sizes, methods adopted for characterization and theoretical studies of m-NFP are provided in the ESI†.

Results and Discussion

X-ray Diffraction and Rietveld Refinement Analysis

The crystallographic structure of all the crystallite sizes of m-NFP have been revealed by synchrotron X-ray diffraction method. In figure 1, we illustrate the XRD pattern of m-NFP with various crystallite sizes, where the observed diffraction pattern corresponds to intrinsic m-NFP phase without any other parasitic phases. The increased level of peak broadening with decrease in the synthesis temperature indicates the reduction in the crystallite size. In figure S1 (ESI), we illustrate XRD patterns for both 80 and 25 nm crystallite sizes and significant differences are observed in the peak width and position. It is interesting to note that the (040) peak being shifted towards larger angle for 25 nm crystallite size as compared with the bulk (80 nm) crystallite sample. Further, we used Williamson Hall relation to estimate the crystallite size and separating the contribution of strain, which dominates at nano scale-level [23]. In figure S2 (ESI), we show the Williamson Hall plot for the representative 25 nm crystallite size sample, where the linear fit and experimental data points lie within the experimental error. The estimated crystallite size from the corresponding XRD pattern has been shown in the figure 1. All the samples are well crystallized in the orthorhombic unit cell with the space group of *Pmnb* belonging to the *maricite* phase [24]. We have made an attempt to obtain crystallite size below 25 nm but ended up with mixed phase contributions (*olivine* and *maricite* phase) and hence, we restricted the lower limit of crystallite size to 25 nm. Similar to olivine phase, m-NFP has orthorhombic unit cell with the four formula units with 4 Na, 4 Fe, 4 P and 16 oxygen atoms occupying the 4a, 4c, 4c, 4c and 8d sites according to the Wyckoff notations [24]. Further, the crystal structures were then refined with the help of Rietveld refinements method by using TOPAS software (ESI), starting the refinement with the initial cell parameters reported in the JCPDS data (File No. 04-012-9665) and literature [24]. Calculated XRD pattern along with the experimental data points and the difference curve are shown in the figure S3 (ESI). Typically, the goodness of fit along with the difference curve decides the fitting quality of the calculated and experimental diffraction pattern. The refinement parameters for bulk and 25 nm crystallite sizes have been given in the Table TS2 (ESI). Unit cell parameters of the lower crystallite sized samples have been obtained with a special effort during the refinement process by considering the errors at the minimal level (up to fourth decimal place). The lattice parameters for the bulk sample from Rietveld refinement are found to be: a = 5.047 Å, b = 6.882 Å and c = 8.994 Å according to the orthorhombic unit cell which is in close agreement with the literature report on the bulk m-NFP sample [25, 26]. Similar procedure has been carried out for estimating the unit cell parameters of other crystallite sizes.

In figure 2(a, b) we illustrate the crystallite size dependent unit cell parameters of m-NFP, which shows significant reduction upon reduction in the crystallite size. It is clear that a monotonic contraction of the lattice parameters from bulk (80 nm) to nanoscale level (25 nm) taking place. We attribute the reduction in the lattice parameters/unit cell volume is due to the combined contribution of (i) lattice strain, (ii) lattice vacancy (here sodium ion vacancies) and (iii) change in bonding characteristics. The magnitude of induced lattice strain upon reduction in crystallite size has been estimated by the Williamson Hall relation and Le bail refinement procedure yields the compressive strain component. The estimated strain values for the 80 nm crystallite size and 25 nm are given in the Table TS2 (ESI), where a significant enhancement has been observed upon reduction of crystallite size.

Additionally, we have quantified sodium ion vacancies in all the crystallite sizes of m-NFP and found to increase with the reduction of crystallite size. The obtained sodium ion vacancies are significantly larger than the earlier reported values on olivine LFP phase with similar crystallite size [27]. The presence of large concentration of Na^+ vacancies in smaller crystallite sizes is not surprising because the low formation energy as well as enhanced surface energy kinetics at the nano scale level. The Na^+ vacancies are charge compensated by the formation of Fe^{3+} ions at the transition metal ion site, i.e. each Na^+ vacancy is responsible for generating Fe^{3+} ion and thereby strong distortion around FeO_6 octahedra. The change in oxidation state of TMs leads to the reduction in Fe-O bond distance resulting in the contraction of the lattice. The lower crystallite sized m-NFP found to have increased concentration of sodium ion vacancies correspondingly more number of hole polarons (Fe^{3+}). The ionic radius of Fe^{3+} being 0.69 Å reduced from 0.77 Å of Fe^{2+} and results into the contraction of the lattice [28]. As listed in the Table TS2 (ESI), the concentration of sodium ion vacancies increased to 14% for 25 nm crystallite size from a minimal value of 0.1% for the bulk m-NFP (80 nm crystallite size). This increase in the sodium ion vacancy concentration leads to the changes in the nearby Fe environment positioned closely along b-direction by changing its oxidation state. Therefore, the reduction in the unit cell parameters is the combined effect of lattice strain (compressive part) and change in the valance state of transition metal ion site (Fe^{3+}) by the Na^+ vacancy. Furthermore, we provide direct evidence for the change in the bonding characteristics upon reduction of crystallite size by using X-ray absorption spectroscopy in the next section.

Electron Microscopy Analysis

Additionally, we have characterized as synthesized m-NFP samples by FESEM and HRTEM techniques to obtain the surface morphology, crystallite size as well as its distribution. In figure 3 (a3, b3 and c3), we illustrate the obtained FESEM images for the representative three different m-NFP samples, which clearly indicates the change in the crystallite size upon reduction of particle size. Further, the surface morphology by FESEM reveal that particles are spherical in shape and uniformly dispersed, whereas the lower-sized samples possesses relatively narrow sized distributions. The HRTEM images reveal the individual particle size distribution as shown in figure 3 (a1, b1, and c1). Furthermore, we have also estimated the average crystallite size and lattice spacing (a2, b2, and c2) for all the samples in the present work which are listed in table TS3 (ESI) along with those values measured by XRD. It is apparent that there is good agreement between the estimated crystallite size values by XRD and HRTEM measurements.

The crystallite size distributions are indicated by yellow circle and we are able to identify only in the case of lower sized sample. On the other hand, in larger sized samples we are unable to distinguish the distribution of crystallites due to larger magnification.

Soft X-ray Absorption Spectroscopy

In figure 4**,** we show the normalized XAS spectra for the Fe L-edge with different crystallite sizes. The spin-orbit coupling results into splitting of the overall spectra into two regions namely L_3 and L_2 edges corresponding to the excitation from the $2p_{3/2}$ and $2p_{1/2}$ levels respectively [29]. Further, the L_3 and L_2 edges are divided into different components depending on the symmetry operation associated with the FeO_6 octahedral structure. The coordination environment of metal ions strongly affects the XAS spectra. The changes in the Fe L-edge spectra with the different symmetry have been observed by various authors [30, 31]. In the case of ideal octahedral geometry, where all the bond length and bond angle are equal leading to a high symmetry configuration. For a perfect octahedral site symmetry (O_h), the d^5 states split into a triplet (t_{2g}) and doublet (e_g) in parallel to the degree of orbital lobs overlap in the direction of ligand atoms. In addition, the splitting of d orbital is mainly governed by the atomic multiplet and crystal field effects [32, 33]. This is typically an elongation of the axial Fe-O bond lengths with the contraction of the equatorial Fe-O bonds lengths. As mentioned in the earlier section, each sodium ion vacancy leads to the formation of Fe^{2+} into Fe^{3+} ion at the transition metal ion site. Hence, it is important to quantify the Fe^{3+} sites in the given crystallite size and substantiate with the extracted XRD Rietveld refinement data. We have carried out care full and systematic analysis by deconvoluting the Fe L edge XAS spectra based on the respective peak positions (Fe^{2+} and Fe^{3+}) and extracted the respective area under the curve. In table TS4 (ESI), we list an estimated relative fraction of Fe^{3+} sites and found to vary with the crystallite size. In addition, the relative fraction of Fe^{3+} sites extracted from XAS spectra are close agreement with the sodium ion vacancy extracted from XRD Rietveld refinement data.

In order to account for the effect of atomic multiplet effects and crystal field splitting, we have simulated the XAS Fe L-edge spectra of transition metal by using the ligand field multiplet theory, which describes the transition of Fe ion from $3d^n$ ground state to $2p3d^{n+1}$ final state. Typically, in atomic multiplet calculations the metal ion environment and local symmetry are described by the ligand field potential. In this work, ligand field multiplet calculations were performed by using a freeware multiplet calculations software CTM4XAS [34]. Initially, we have attempted to simulate the experimental spectra by considering the perfect octahedral symmetry (O_h) with choosing the various crystal field splitting parameters but it was unsuccessful. Though the spectral features are similar to the octahedral symmetry in appearance, we were able to obtain an identical simulated spectrum only with the D_{3d} symmetry. This particular symmetry operation corresponds to the distorted octahedral geometry and similar distortions was found in polyanionic compounds like $NaMO_2$ [35, 36]. The earlier investigations on the similar structure (D_{3d}) suggest that the FeO_6 stabilized in distorted octahedral geometry with the different type of bond lengths. In addition, the recent studies on O-LFP suggests that the MO_6 octahedron has two types of bond length with three shorter and three longer bond lengths form a distorted octahedral symmetry [28, 37]. The trigonal distortion results in splitting of the degenerate t_{2g} level further into two groups namely a singlet a_{1g} and a doublet e_g^{π} component, summing into the overall three set of energy levels in the 3d orbitals [37]. Thus, with the multiplet calculations and by comparison of experimental data, we are able to provide a complete set of physical parameters that defines the evolution of electronic structure of m-NFP. Remarkably, the deconvoluted L_3-edge spectra for the 80 nm sample reveal the three different contributions shown in figure S4 (ESI). Similarly, we have carried out deconvolution of L_3-edge with three components for all the crystallite sizes down to 25 nm. From the simulated spectra, we were able to extract the crystal field strength (the energy separation between the t_{2g} (π) and e_g (σ) level) for all the crystallite sizes.

Similar to the ideal octahedral geometry, in the present case the 10 Dq value signifies the difference between the t_{2g} (π) component (chosen as the centre of a_{1g} (π) and e_g (π) components) and e_g (σ) component belonging to the D_{3d} symmetry. In figure S5 (a and b; ESI), we illustrate the experimental curve fitted with simulated spectra for the representative 80 nm and 25 nm crystallite size. In addition to 10Dq value, the parameter related to the D_{3d} symmetry contributing the Fe L-edge spectra are the distortion parameters D_σ and D_τ. The conversion of O_h to D_{3d} symmetry group is the result of trigonal distortion in the structure which changes the bond lengths and bond angles of the FeO_6 octahedra. The D_σ and D_τ parameters signifies the same meaning as the D_s and D_t in the tetragonal distortion. Another way of considering the distortion in the spectrum is the result of splitting of the t_{2g} orbital in the spectra. These two parameters are extracted from the simulation and listed in the table TS4 (ESI). Combining these parameters, we can define the distorted trigonal field ($D^0_{trig.}$) in terms of the D_σ and D_τ as [38]:

$$D^0_{trig} = -3D_\sigma - \frac{20}{3}D_\tau \qquad (2)$$

The calculated trigonal field with the help of above extracted parameters for different crystallite sizes of m-NFP are listed in the table TS4 (ESI). As we can see from the table TS4, trigonal field increases continuously with reduction in the crystallite size and hence increasing the contribution of a_{1g} in the spectrum. If we define the internal t_{2g} splitting as Δ, which is the difference between the a_{1g} (π) and e_g (π) orbitals then one can specify the energy of difference of orbitals in Fe 3d in the form of 10Dq and Δ. The energy for the three components in the Fe L_3 edge can be written as [38]

$$E\ (e_g\ (\sigma)) = 6Dq \tag{3}$$

$$E\ (e_g\ (\pi)) = -4Dq+\frac{1}{3}\Delta \tag{4}$$

$$E\ (a_{1g}\ (\pi)) = -4Dq-\frac{2}{3}\Delta \tag{5}$$

The above equations has been written with the assumption of a_{1g} being the lowest energy level. Depending on the above parameters defined for the D_{3d} symmetry of the spectra, the various energy levels have been extracted using 10Dq and Δ from the deconvoluted spectra of all the crystallite sizes and are listed in the table TS5 (ESI).

As the crystallite size decreases from 80 to 25 nm, one can observe that the contribution of the a_{1g} component increases which is related to the distortion of the octahedral geometry. The energy of the a_{1g} component decreases in the energy along with the energy of the e_g (π) component where it is shifting downwards resulting in the overall increase in the Δ value. The parameter 10Dq is considered from the simulation directly and the value of Δ has been estimated from the deconvolution of the spectra. The distortion parameters in the table TS4 (ESI) show that the parameter D_σ increases with the decrease in the crystallite size whereas D_τ component decreases continuously and approaches to zero. The parameter listed in the Table TS4 (ESI) signifies that the trigonal distortion field on the octahedral structure increases with the decrease in the crystallite size. Further, the trigonal distortion changes the bond length in the octahedral structure deviating it from the ideal octahedral symmetry. Additionally, we have estimated the energy of the various components involved in the spectra. Overall, the quantities derived from the present study (both XRD and XAS) reveal that the bond lengths associated with octahedra decreases with the reduction of the crystallite size.

Additionally, we have obtained the oxygen K-edge spectra of all the crystallite sizes of m-NFP as shown in figure S6 (ESI). The whole spectra are divided into two regimes namely the pre-edge and post edge spectral features, the changes in the pre-edge region is significant as compared to the post edge region with the decrease in the crystallite size. In Fe based system, the pre-edge region is mainly the contribution of the unoccupied 3d metal state hybridized with the ligand 2p orbitals whereas the features in post-edge region are dominated by the contribution from the metal 4sp orbitals mixed with the oxygen 2p orbitals [39, 40]. Clearly, the changes in the pre-edge spectral feature around 530 eV with respect to different crystallite sizes are visible. According to the literature, the pre-edge region consists of the three components for the D_{3d} symmetry [41]. Whereas in octahedral symmetry group, the pre-edge region splits into two peaks namely t_{2g} and e_g whose intensity ratio is related to the number of unoccupied states in the corresponding orbitals. Unlike the Fe L-edge spectra where all the three features are clearly visible, here only two features are visible in the oxygen 1s spectra. We consider the first feature is the combination of the a_{1g} and e_g (π) features whereas the second feature is purely the contribution of the e_g (σ) component. As seen in the Fe L-edge spectra the distortion in the octahedral site results the increase of the a_{1g} spectral feature, the similar behaviour with the crystallite size can be seen in the pre-edge region. The contribution of the two components namely t_{2g} and e_g are separated by the deconvolution, correspondingly the 10Dq and the intensity ratio of the two components are estimated and depicted in the figure 5**.** As seen in the figure 5, the intensity ratio of t_{2g} to e_g increases with the reduction in the crystallite size which can be seen for the case of Fe L-edge as well. The increase in the intensity ratio is attributed to the enhanced trigonal distortion in the octahedral geometry. With the decrease in crystallite size the contribution due to the unoccupied t_{2g} orbitals increases along with the separation between the two components caused by the trigonal distortion. It is interesting to note that the increased level of intensity ratio (t_{2g}/e_g) indicates that the less oxygen 2p states to hybridize with 3d-states implying enhanced level of covalency and decrease in the unit cell parameters [42]. The reduction in the crystallite size, the 10Dq value increases and it represents the enhancement in the splitting due to the destabilization of the e_g orbitals where the charge is transferred from the ligand to metal d level. Hence, all the studies related to the structural changes support the increased distortion in the octahedral symmetry with the reduction of the crystallite size.

DFT Calculations

Further, we have performed DFT calculation to compute the structural changes in m-NFP with different crystallite sizes. For this purpose, we have optimized the unit cell and geometry using the GGA+U functional. We varied the U value and obtained the optimized unit cell parameters for the bulk m-NFP crystal structure. With an increase of U value, the Columbic repulsion between the two transition metal sites increases and subsequently elongation of the unit cell has been observed [43]. According to the structural arrangement of m-NFP, FeO_6 octahedron is placed along the *b*-direction and with an increase in the U value more elongation is observed along the *b*-direction as compared to the *a*- and *c*-direction. Considering the band gap value and the unit cell parameters, the value of $U_{eff} = U-J = 5.0$ eV for Fe has been chosen. Based on the chosen U value and various structural parameters as listed in Table TS6 (ESI), we optimized crystal and electronic structure of m-NFP for different crystallite sizes. The estimated lattice parameters for the zero Na vacancy concentration with this U_{eff} value are close to those observed from the Rietveld refinement analysis on the XRD pattern of bulk (80 nm) crystallite size as well as the earlier reports on m-NFP [25, 44].

In figure 6 (a & b), we illustrate the calculated lattice parameters for m-NFP with different concentration of sodium vacancies. Increase in the concentration of sodium vacancies lead to the reduction in the unit cell parameters and volume. In figure 6(c), we show the isolated FeO_6 octahedron taken from the optimized cell structure with the introduction of different concentration of Na vacancies in the structure. For example, the octahedra shown in the left side of box in the figure 6 (c) is extracted from the structure without Na vacancy (80 nm) whereas the octahedra depicted in the right side of the figure 6(c) represents the octahedral structure with the highest number of sodium vacancies (14.2 %) in the structure. Clearly, these images illustrate the three types of bond lengths and each octahedron is extracted from the individual super cell structures with different level of Na vacancies. The overall observed trend for the unit cell parameters is similar to the experimental results discussed in the previous section, where the average bond length decreases with increasing density of Na vacancies from its initial value of 2.243 Å to 2.101 Å showing the overall contraction illustrated in figure 6 (d). The contraction in the bond lengths with Na vacancy is similar to the contraction observed in the olivine phosphate structure [37, 45]. We observe an overall decrease in the bond length of about 6%, which is similar to the previous reports on olivine LFP structure [37, 45]. Hence, the decrease in the lattice parameters is the direct consequence of increased concentration of polaronic sites (Fe^{3+}) in the structure, i.e. due to the sodium vacancies.

The lattice contraction/elongation of Fe-O strongly depends on the electron occupation in the transition metal d orbital prior to withdrawal. In m-NFP structure, it is clear that the transition metal ion stays in the quasi octahedral geometry with the oxygen. For the present case we noticed three types of bond lengths in the structure with the average bond length of 2.243 Å for zero Na vacancy concentration. Remarkably, an increase in the Na vacancies leads to reduction in the average bond length to 2.101 Å for 14.2 %. We attribute the reduction in the lattice parameters in m-NFP structure is mainly determined by the change in the surroundings of octahedral transition metal ion. Hence, the difference between the bond lengths of FeO_6 octahedron is due to the difference between the respective orbital occupations. It is usually believed that the transition metal oxides exhibit the lattice expansion with the reduction in the crystallite size or particle size [46].

The previous theoretical studies on the olivine structure revealed that the coupling of the alkali ion vacancy with the hole polaron in the structure [28]. In addition, we made an attempt to explore the effect of isolated charged Na^+ vacancy (without any hole formation) in the structure. By simply removing a sodium atom from the structure, simultaneously an electron also gets removed from a Fe site with the creation of a hole-polaron (here Fe^{2+} becomes Fe^{3+}; results of Fig. 6) in the structure and the vacancy is termed as the neutral vacancy. In order to study the effect of charged sodium vacancy, we removed a sodium atom from the structure followed by the addition of a homogeneously-distributed electron into the structure which is hereafter called as charged vacancy without any hole-polaron formation. In this case, we introduced the charged vacancy in the similar concentration as the neutral vacancy incorporated previously. The effect of charged vacancy concentration on the unit cell parameters is shown in figure 7. As we can see from the figure 7, the cell volume shows an expansion continuously with the increase in the concentration of the charged vacancy which is exactly opposite to the case of neutral vacancy behaviour and the experimental results. Hence, we confirm that the lattice contraction observed in the experimental result is the effect of neutral Na vacancy with the hole polaron formation.

In summary, m-NFP with various crystallite sizes has been synthesized by the conventional solid state route without any parasitic phases. The phase formation and the purity of m-NFP have been confirmed with the XRD analysis followed by X-ray absorption spectroscopy measurement. The Rietveld refinement analysis on the XRD data reveal that the reduction in the unit cell parameters with the decrease in crystallite size due to the combined effect of Na vacancy and change in bonding character. Further, the structural analysis has been done in detail with the X-ray absorption spectroscopy for examining the changes in the bonding character with crystallite size. The structural studies indicate the increase in the disorder in the lattice by the sodium ion vacancies with the decrease in crystallite size. The increase in distortion with the reduction in crystallite size is explained in terms of changes in the hybridization of Fe-O bonding character. Additionally, we ascertained the atomic structure of m-NFP by using the DFT calculations within the GGA+U framework, which directly reveal the nature of the local distortion associated with the transition metal ion. Additionally, we have explored the m-NFP atomic structure with the variation in the Na vacancy concentration, where there is excellent agreement between the calculated atomic structure and the corresponding experimental results. The lattice contraction observed with the size reduction is related to the distortion in the m-NFP structure occurring due to the polaron formation.

ASSOCIATED CONTENTS

Supporting Information:- The experimental methods such as synthesis of m-NFP nano crystals, characterization techniques, Rietveld refinement analysis, supporting figures, and DFT calculations are provided in the supplementary information.

AUTHOR INFORMATION

Corresponding author

Email: murug@physics.du.ac.in

Notes

The authors declare no competing financial interest.

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