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# Insights into structure, morphology and conductivity of the earth-abundant NASICON phosphate, $\text{Na}_4\text{MnFe}(\text{PO}_4)_3$ †

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Phosphate-based NASICON materials are an excellent candidate for both electrode and solid electrolyte materials in sodium-ion batteries (SIBs). The development of new NASICON materials with higher ionic and electronic conductivities based on low cost and abundant elements is necessary for advancement of SIBs. In this study, we report the structure, morphology and conductivity of the earth-abundant Mn/Fe-based NASICON phosphate  $\text{Na}_4\text{MnFe}(\text{PO}_4)_3$ . Pure phase powders were synthesized by solution-assisted solid-state reaction, sol-gel and Pechini methods. From refined X-ray diffraction data, the prepared phosphate was found to crystallize in trigonal symmetry with space group  $R\bar{3}c$ . The effect of synthesis method on microstructure and conductivity was investigated using scanning electron microscopy (SEM), atomic force microscopy (AFM) and impedance measurements. Smaller particle size and regular distribution of the powder was designed using a Pechini route. Impedance measurement showed a notable enhancement in conductivity, from  $0.543 \times 10^{-7}$  to  $1.52 \times 10^{-7} \text{ S cm}^{-1}$  at  $30^\circ\text{C}$ , when the powder synthesis method was altered from a solution-assisted solid-state reaction to the Pechini route, highlighting the remarkable effect of the synthesis method on conductivity.

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## 1. Introduction

In recent decades, the global energy transition to renewable energy and technological advancements have caused a significant demand for energy storage devices. Rechargeable batteries, particularly lithium-ion batteries (LIBs), play a crucial role in energy storage fields owing to their long cycle life and high energy density.<sup>1–5</sup> Nevertheless, the unequal geographical distribution and skyrocketing price of lithium resources restrict LIB technology from being used indefinitely, especially in large-scale energy storage applications that require a large quantity of active material.<sup>6,7</sup> To overcome this limitation, earth-abundant alternative technologies should be developed. For instance, sodium ion batteries (SIBs) can be a sustainable alternative to LIBs due to the low cost and earth abundance of sodium, as well

as their electrochemical properties that are comparable to that of LIBs.<sup>7–9</sup>

In this regard, numerous efforts have been made to develop new efficient components (electrode and electrolyte) for SIBs. NASICON-type polyanionic compounds are one of the most important candidates for use in both electrodes and electrolytes applications in SIBs, thanks to their 3D open framework that provides a large migration channel for  $\text{Na}^+$ .<sup>10,11</sup> Recently, NASICON phosphates with general formula  $\text{Na}_{3+x}\text{MnM}(\text{PO}_3)_4$  ( $\text{M}$  = transition metal) has been intensively researched, especially as cathode material owing to the environmental-friendly and cost-effective of Mn, as well as the high redox voltage of  $\text{Mn}^{2+/3+}$  (3.6 V) and  $\text{Mn}^{3+/4+}$  (4.0 V).<sup>12–18</sup> To date, a variety of Mn–M combinations ( $\text{M}$  = transition metals) in NASICON structure have been developed such as,  $\text{Na}_4\text{MnCr}(\text{PO}_4)_3$ ,<sup>14</sup>  $\text{Na}_4\text{MnV}(\text{PO}_4)_3$ ,<sup>15</sup>  $\text{Na}_4\text{MnAl}(\text{PO}_4)_3$ ,<sup>16</sup>  $\text{Na}_3\text{MnTi}(\text{PO}_4)_3$ ,<sup>17</sup> and  $\text{Na}_3\text{MnZr}(\text{PO}_4)_3$ .<sup>18</sup> On the other hand, Fe-based NASICON materials, such as  $\text{Na}_3\text{Fe}_2(\text{PO}_4)_3$ , have also been largely studied as a promising electrode materials for SIBs because of their high structural stability and low production cost.<sup>19–22</sup> These considerations make the investigation of novel Mn/Fe-based phosphates an attractive idea. Additionally, it is reported that the synergistic effect of Mn–Fe in polyanionic compounds improves thermal stability and generates an increase in the redox potential of Fe.<sup>23,24</sup>

In fact, the development of new electrode materials with higher ionic and electronic conductivities is essential for enhanced the electrochemical properties in SIBs. Various

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strategies were adopted to improve the conductivity in the NASICON structure, *e.g.*, particle design, doping and carbon coating.<sup>10</sup> It is worth noting that the conductivity of the material can also be influenced by different factors, such as the morphology of the particles<sup>25,26</sup> and the presence of secondary phases.<sup>27</sup> In this context, several works were reported on the design of suitable particle morphology and carbon coating *via* various techniques towards high electrochemical performance.<sup>9,25,26</sup>

Based on the above considerations, we report the structural, morphological and conductivity investigations of an earth-abundant Mn/Fe-based NASICON phosphate with 4 Na per formula unit, Na<sub>4</sub>MnFe(PO<sub>4</sub>)<sub>3</sub> (denoted as NMFP). To the best of our knowledge, the synthesis of this compound was reported as single crystal and no structural data were provided.<sup>28</sup> For the first time in this work, we employed three methods, *i.e.*, solution-assisted solid-state reaction, sol-gel and Pechini to synthesize NMFP pure powders and investigated the effect of synthesis methods on the structural, morphological and conduction properties by combining X-ray diffraction (XRD), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), atomic force microscope (AFM) and impedance spectroscopy.

## 2. Experimental section

### 2.1. Materials preparation

**2.1.1 NMFP powder synthesis.** NMFP was prepared by a solution-assisted solid-state reaction, a simple sol-gel and Pechini methods. Na<sub>2</sub>NO<sub>3</sub> (99.4%, VWR Chemicals), MnCO<sub>3</sub> (99.9%, Alfa Aesar), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (≥99.0% AnalaR NORMA-PUR) and NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> (99.9%, Acros Organics) are used as starting reagents in 2 : 1 : 1 : 3 molar ratios, respectively. In each method, firstly, a solution A was prepared from a mixture of Na<sub>2</sub>NO<sub>3</sub>, MnCO<sub>3</sub>, and Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O dissolved in 60 ml of distilled water with 8 ml of HNO<sub>3</sub> and kept 1 h in stirring under heating at 60 °C.

For the solution-assisted solid-state reaction, solution B was prepared by dissolving NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> in 50 ml of distilled water and added to the first solution. The obtained solution was stirred at 80 °C for 3 h and heated overnight to evaporate water. The resulting precipitate was dried at 120 °C for 6 h and calcined at 400 °C and 700 °C for 24 h each in an air atmosphere, with a heating rate of 10 °C min<sup>-1</sup>. Subsequent to each calcination step, the powder was cooled and reground in an agate mortar.

In the case of sol-gel method, a second solution B' was prepared by dissolving NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub> and citric acid with the molar ratio (Na<sup>+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>): citric acid (≥99%, VWR Chemicals) = 1 : 1 in 50 ml of distilled water. Then, the solution A + B' was stirred at 80 °C for 3 h. After that, the final solution was heated overnight to form a gel. The obtained gel was dried at 120 °C for 6 h and underwent the same heat treatment applied for the solution-assisted solid-state method.

For the Pechini route, in addition to the solution B' was prepared in case of sol gel, another solution C was prepared by dissolving ethylene glycol (≥99.5%, Panreac) in 10 ml of

distilled water in molar ratio ethylene glycol : citric acid = 4 : 1. The mixed solution A + B' + C was stirred at 80 °C until a solid gel was formed. The obtained gel was dried at 120 °C for 24 h before being sintered under the same temperatures as those outlined in the solution-assisted solid-state method.

### 2.1.2 Pellets preparations

For the measurement of the complex impedance, a solution with 2 wt% PVA was prepared, each prepared powder was ground in agate mortar with 20 wt% of this solution as a binder and pressed into pellets of 13 mm in diameter with a pressure of 8 MPa for 3 min. Then, the pressed pellets were sintered at 500 and 710 °C for 4 and 12 h, respectively, with a heating rate of 5 °C min<sup>-1</sup>. The obtained pellets were covered with silver lacquer to guarantee good electrical contact between the pellet and the electrodes.

### 2.2. Materials characterization

The purity of the synthesized powders was analyzed by X-ray diffraction (XRD) at room temperature, using a Rigaku SmartLab X-ray Diffractometer operating in the 2θ range of 10° ≤ 2θ ≤ 100° with a 0.02° step and a 5° min<sup>-1</sup> scan rate. The obtained powder diffraction patterns were analyzed and refined by Rietveld refinement approach using FullProf Program,<sup>29</sup> based on the crystallographic information file (CIF) of Na<sub>4</sub>MnV(PO<sub>4</sub>)<sub>3</sub>.<sup>8</sup> The structural visualization was carried out using Diamond software.<sup>30</sup> The morphology and the chemical composition of the synthesized samples were observed and analyzed using a scanning electron microscope (QUATTRO S-FEG-ThermoFisher scientific) coupled with an energy-dispersive X-ray spectroscopy (EDS) analyzer. The Archimedeian method was used to calculate the density of the sintered pellets using distilled water as a suspension medium. The surfaces of the pellets were observed using Atomic Force Microscope (CorreAFM). The infrared spectroscopy spectra of the powder samples were obtained using FT-IR spectrometer (PerkinElmer RX-I model), covering a frequency range of 400–4000 cm<sup>-1</sup>. Differential scanning calorimetry (DSC) measurement was carried out by Shimadzu DSC-60 Plus within a 45–300 °C temperature range in the atmosphere with a heating rate of 10 °C min<sup>-1</sup>.

### 2.3 Impedance measurements

The impedance measurement was carried out at different temperatures (RT–150 °C) in the frequency range from 1 Hz to 1 MHz using Solartron analytical Modulab Xm MTS device coupled to Linkam cell, and the data was fitted using the ZView software. The ionic conductivity (σ) and the activation energy (E<sub>a</sub>) were derived from impedance data using eqn (1) and (2), respectively.

$$\sigma = \frac{L}{RS} \quad (1)$$

where *L* = pellet thickness, *S* = surface area of the electrode placed on the pellet and *R* = resistance value.



$$\sigma = A \exp\left(\frac{-E_a}{KT}\right) \quad (2)$$

where  $A$  = pre-exponential factor,  $T$  = absolute temperature,  $K$  = Boltzmann constant.

### 3. Results and discussion

#### 3.1 Structural and morphological description

The NMFP samples prepared by solution-assisted solid-state reaction, sol-gel and Pechini routes denoted as NMFP/SS, NMFP/SG and NMFP/P, respectively, crystallize in a NASICON structure with  $R\bar{3}c$  space group. The Rietveld refined powder X-ray diffractograms of NMFP/SS, NMFP/SG and NMFP/P are illustrated in Fig. 1a–c. The Rietveld refinement of the three samples exhibits a good correlation between the calculated and the experimental XRD patterns with good weighted profile  $R$ -factor, which confirms the formation of the Trigonal NASICON pure phase with  $R\bar{3}c$  space group. A negligible difference is observed between the obtained crystallographic data of the

three powders. The refinement details of the three powder XRD patterns are listed in Table 1.

The crystal structure created from CIF file of NMFP/SG is illustrated in Fig. 1d. This structure is built by edge-sharing  $\text{MnO}_6/\text{FeO}_6$  octahedra and  $\text{PO}_4$  tetrahedra forming a basic constituent known as ‘lantern unit’, leading to the 3D-dimensional open framework. In this structure, Na atoms occupied two types of interstitial sites with different oxygen coordination environments: Na1 site in the  $6b$  Wyckoff position (100% occupied) with sixfold coordination and Na2 site in  $18e$  Wyckoff position (100% occupied) with eightfold coordination. Fe and Mn atoms occupy octahedral environment by sharing the  $12c$  Wyckoff position with 50% occupancy per each. The bond-valence model (BVS) (Brown & Altermatt)<sup>31</sup> was applied to all three samples. The BVS values calculated for Na1, Na2, and P1 are approximately 1.1, 0.9, and 5.0, respectively, which are close to the expected oxidation states, *i.e.*,  $\text{Na}^{1+}$  and  $\text{P}^{5+}$ . The mixed Mn/Fe site shows a total BVS value of  $2.7 + 2.5 = 5.2$ , which is close to the sum of  $\text{Mn}^{2+}$  and  $\text{Fe}^{3+}$  oxidation states. However, to accurately confirm the exact oxidation state of each element, further characterization techniques are required, such

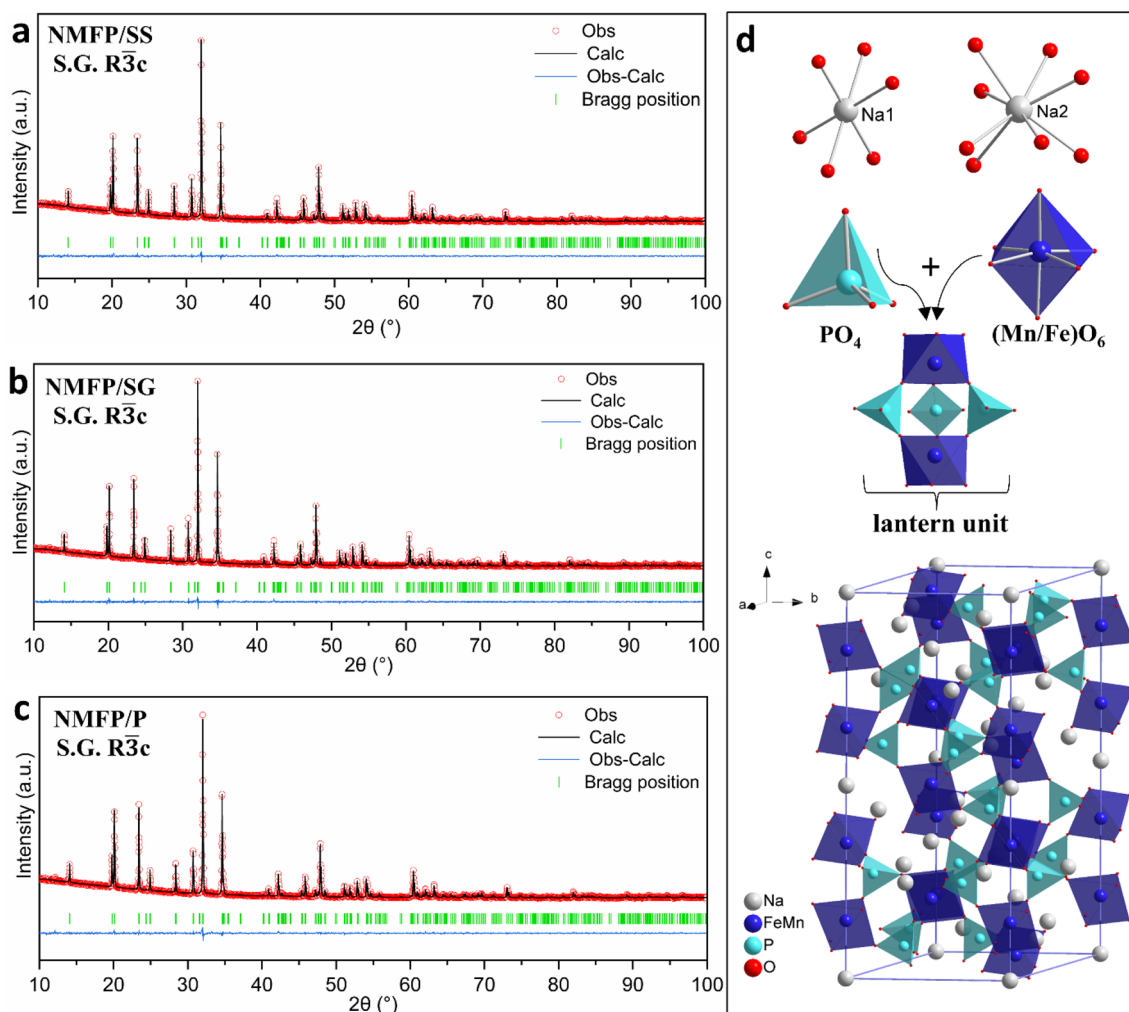


Fig. 1 (a–c) Rietveld refinement of NMFP powders, (d) visual representation of Na1, Na2, Mn/Fe and P atoms environments and NMFP unit cell.

Table 1 Rietveld refinement data of NMFP synthesized by different methods

Crystal data			
Synthesis method	SS	SG	P
Chemical formula	Na <sub>4</sub> MnFe(PO <sub>4</sub> ) <sub>3</sub>	Na <sub>4</sub> MnFe(PO <sub>4</sub> ) <sub>3</sub>	Na <sub>4</sub> MnFe(PO <sub>4</sub> ) <sub>3</sub>
<i>M<sub>r</sub></i> (g mol <sup>−1</sup> )	487.66008	487.66008	487.66008
Crystal system, space group	Trigonal, <i>R</i> $\bar{3}c$	Trigonal, <i>R</i> $\bar{3}c$	Trigonal, <i>R</i> $\bar{3}c$
Temperature (K)	289	289	289
<i>a</i> , <i>c</i> (Å)	8.96603 (7), 21.4326 (2)	8.96068 (6), 21.44306 (18)	8.96746 (9), 21.4345 (3)
<i>V</i> (Å <sup>3</sup> )	1492.13 (2)	1491.07 (2)	1492.74 (3)
<i>Z</i>	6	6	6
Radiation type	X-ray, Cu Kα ( <i>λ</i> = 1.5406 Å)		
<b>Data collection</b>			
Diffractometer	Rigaku SmartLab		
2θ values (°)	2θ <sub>min</sub> = 10.01 2θ <sub>max</sub> = 100.01 2θ <sub>step</sub> = 0.02		
<b>Refinement</b>			
<i>R</i> factors and goodness of fit	<i>R<sub>p</sub></i> = 2.354, <i>R<sub>wp</sub></i> = 2.987, <i>R<sub>exp</sub></i> = 2.689, <i>R<sub>Bragg</sub></i> = 4.432, <i>χ</i> <sup>2</sup> = 1.234	<i>R<sub>p</sub></i> = 2.376, <i>R<sub>wp</sub></i> = 3.052, <i>R<sub>exp</sub></i> = 2.704, <i>R<sub>Bragg</sub></i> = 5.062, <i>χ</i> <sup>2</sup> = 1.273	<i>R<sub>p</sub></i> = 2.346, <i>R<sub>wp</sub></i> = 2.986, <i>R<sub>exp</sub></i> = 2.686, <i>R<sub>Bragg</sub></i> = 4.343, <i>χ</i> <sup>2</sup> = 1.235
No. of parameters	94	94	94
No. of data points	4501	4501	4501

as XPS measurements. The details of atomic positions, isotropic displacement parameters and BVS calculation of NMFP materials are given in Table 2. The selected bond distances and the atomic angles are summarized in Table S1.† Similar to other NASICON phosphates, Na(2)–O distances are found to be higher than the Na(1)–O distances, leading to an easier extraction of Na<sup>+</sup> from the Na2 site compared to the Na1 during the redox reaction.<sup>15,32</sup>

The surface morphology and elemental composition of NMFP/SS, NMFP/SG and NMFP/P powders were analyzed by electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The grain size distribution of the powders is

shown in Fig. 2a, the morphology of NMFP/SS, NMFP/SG and NMFP/P powders indicates the formation of nearly round-shaped and polygonal grains. From the histograms plotted in Fig. S1a† determined through analysis with the ImageJ software, a significant difference in particle size can be observed between the three powders. The grain size of NMFP/SS powder is irregular, characterized by the presence of larger particles with sizes approaching 8 μm and smaller grains with equivalent diameters ranging from about 1 to 6 μm. While the NMFP/SG and NMFP/P powders have uniform rounded-shape particles with sizes of around 1–4 μm and average grain sizes of 2.45 and 1.81 μm for NMFP/SG and NMFP/P respectively. This

Table 2 Atomic positions, isotropic displacement parameters (Å<sup>2</sup>) and BVS calculation of NMFP synthesized by different methods

	Method	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>iso</sub>	Occ. (<1)	BVSum
Na1	SS	0.00000	0.00000	0.00000	0.020 (2)		1.143 (6)
	SG	0.00000	0.00000	0.00000	0.017 (2)		1.105 (5)
	P	0.00000	0.00000	0.00000	0.018 (3)		1.118 (5)
Na2	SS	−0.3333	−0.0267 (5)	0.08330	0.0340 (16)		0.952 (5)
	SG	−0.3333	−0.0277 (5)	0.08330	0.0363 (15)		0.952 (4)
	P	−0.3333	−0.0275 (5)	0.08330	0.0310 (16)		0.949 (5)
Fe	SS	0.00000	0.00000	0.14962 (8)	0.0087 (8)	0.50000	2.554 (13)
	SG	0.00000	0.00000	0.14932 (8)	0.0102 (8)	0.50000	2.567 (12)
	P	0.00000	0.00000	0.14940 (9)	0.0087 (9)	0.50000	2.554 (13)
Mn	SS	0.00000	0.00000	0.14962 (8)	0.0087 (8)	0.50000	2.777 (14)
	SG	0.00000	0.00000	0.14932 (8)	0.0102 (8)	0.50000	2.791 (13)
	P	0.00000	0.00000	0.14940 (9)	0.0087 (9)	0.50000	2.777 (14)
P	SS	−0.3333	−0.3674 (3)	0.08330	0.0118 (12)		5.015 (30)
	SG	−0.3333	−0.3682 (3)	0.08330	0.0095 (11)		5.097 (30)
	P	−0.3333	−0.3676 (3)	0.08330	0.0114 (13)		5.067 (31)
O1	SS	0.1951 (5)	0.2083 (5)	0.19238 (16)	0.0129 (16)		
	SG	0.1963 (5)	0.2084 (5)	0.19292 (17)	0.0180 (16)		
	P	0.1962 (5)	0.2075 (5)	0.19263 (18)	0.0180 (18)		
O2	SS	0.1857 (4)	0.0149 (6)	0.0844 (2)	0.0085 (13)		
	SG	0.1853 (4)	0.0148 (5)	0.0853 (2)	0.0086 (12)		
	P	0.1857 (4)	0.0144 (6)	0.0848 (2)	0.0087 (13)		





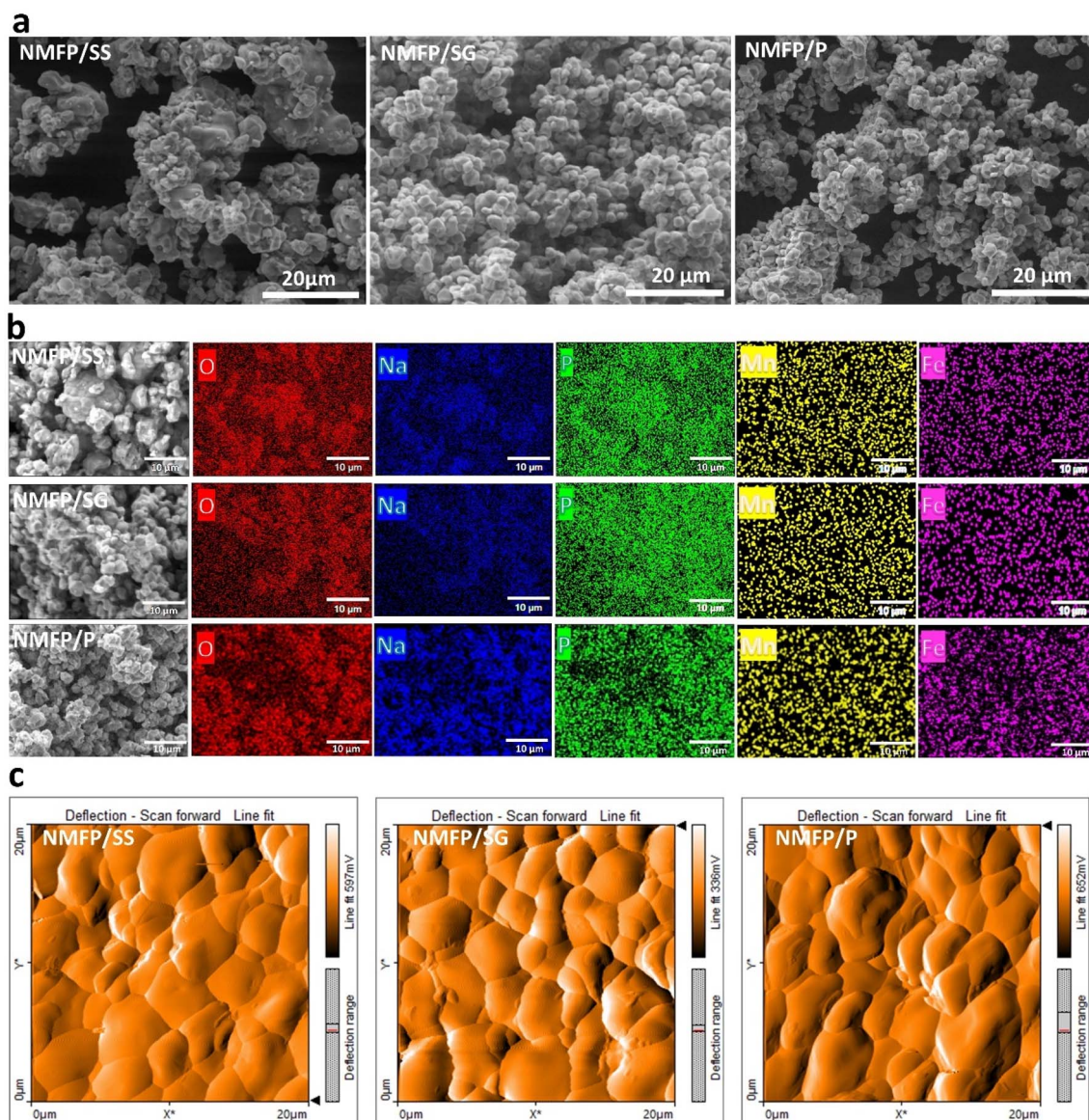


Fig. 2 (a) SEM images and (b) EDS elemental mapping images of NMFP powders. (c) AFM surface images of NMFP pellets sintered at 710 °C.

Table 3 Density of NMFP pellets

Pellets	Theoretical density (g cm <sup>-3</sup> )	Relative density (%)
NMFP/SS	3.256	92.260
NMFP/SG	3.259	93.568
NMFP/P	3.255	97.907

observation explained by the impact of the synthesis method on particle size. The sol-gel and the Pechini methods tend to produce smaller and regular grains than the solid-state method.<sup>33,34</sup> The EDS mapping presented in Fig. 2b confirms the homogeneous distribution of Na, Mn, Fe in the three powders. The EDS spectra (Fig. S2†) of the different powders confirm the existence of Na, Fe, Mn, P and O elements with atomic ratios very near to expected stoichiometric composition,

*i.e.*, Mn/Fe ratios are 1.14, 1.16, 1.15 for NMFP/SS, NMFP/SG and NMFP/P, respectively, which is in good agreement with powder diffraction data.

Fig. 2c, shows the surface images of pellets sintered at 710 °C using Atomic Force Microscope (AFM). The theoretical and relative density determined by Rietveld refinement and Archimedian method are listed in Table 3. All the samples show a high relative density (>90%). The NMFP/P pellet possess the highest density of ~97.91%, while NMFP/SS pellet has the lower density of ~92.26%. These findings are further supported by AFM images, where the grains appear more densified passing from NMFP/SS to NMFP/P pellet. The average grain size of sintered pellets was determined using ImageJ software based on AFM images (Fig. S1b†). Values of 3.89, 3.33, and 3.47 μm were obtained for the NMFP/SS, NMFP/SG and NMFP/P pellets, respectively. The observed increase in grain size compared to

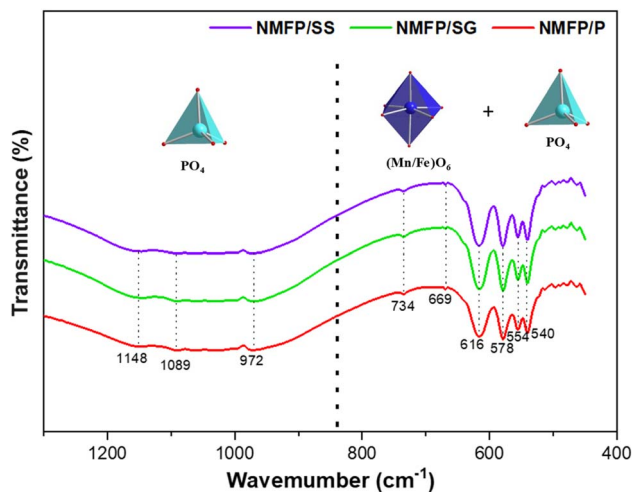


Fig. 3 FT-IR spectrum of the NMFP synthesized by the three routes.

the pristine powders is explained by particle growth with heat treatment at 710 °C.

### 3.2. FT-infrared spectroscopy

The FTIR spectra of the three powders are presented in Fig. 3. It appears that all samples exhibit FTIR spectra with identical

band positions and similar intensities. The absorption bands at  $\sim 554$ , 669 and  $734\text{ cm}^{-1}$  can corresponds to the bending/stretching of Mn/Fe–O bond in Mn/FeO<sub>6</sub> octahedra.<sup>35,36</sup> The rest of the bands observed around 970–1200  $\text{cm}^{-1}$  and 400–600  $\text{cm}^{-1}$  corresponds to [PO<sub>4</sub>]<sup>3−</sup> stretching:  $\nu_3$  (PO<sub>4</sub>) = 1148  $\text{cm}^{-1}$ , 1089  $\text{cm}^{-1}$ ;  $\nu_1$  (PO<sub>4</sub>) = 972  $\text{cm}^{-1}$ ;  $\nu_4$  (PO<sub>4</sub>) = 616  $\text{cm}^{-1}$ , 578  $\text{cm}^{-1}$ , 540  $\text{cm}^{-1}$ .<sup>35,37,38</sup> These results are in good agreement with the reported literature of NASICON phosphates.<sup>35</sup>

### 3.3 Impedance study

To investigate the impact of synthesis method on the electrical properties of NMFP compound, impedance spectroscopy was performed on the three pellets. Fig. 4a shows the complex impedance curves of NMFP/SS, NMFP/SG and NMFP/P pellets at 30 °C. The Nyquist plot of the three samples exhibits three different regions depending on the frequency. The first region at a higher frequency shows a depressed semicircular arc corresponding to the grain response, represented by sub-equivalent circuit resistance ( $R_G$ )/constant phase element (CPE1). The second region at intermediate frequency shows an incomplete semicircle representing the grain boundary behavior, described by a sub-equivalent circuit resistance ( $R_{GB}$ )/constant phase element (CPE2). This region is clearly

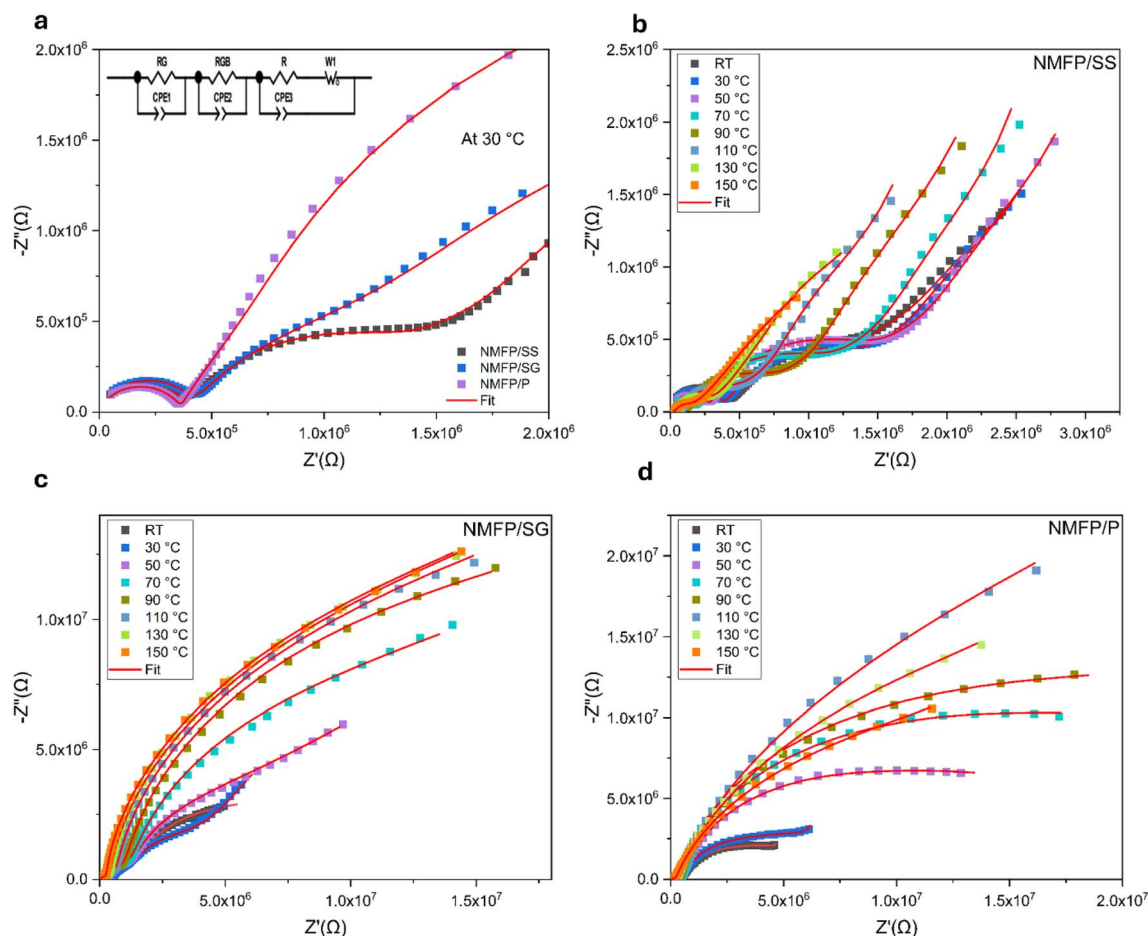


Fig. 4 Nyquist curves of NMFP/SS, NMFP/SG and NMFP/P pellets (a) at 30 °C and (b–d) at different temperature.



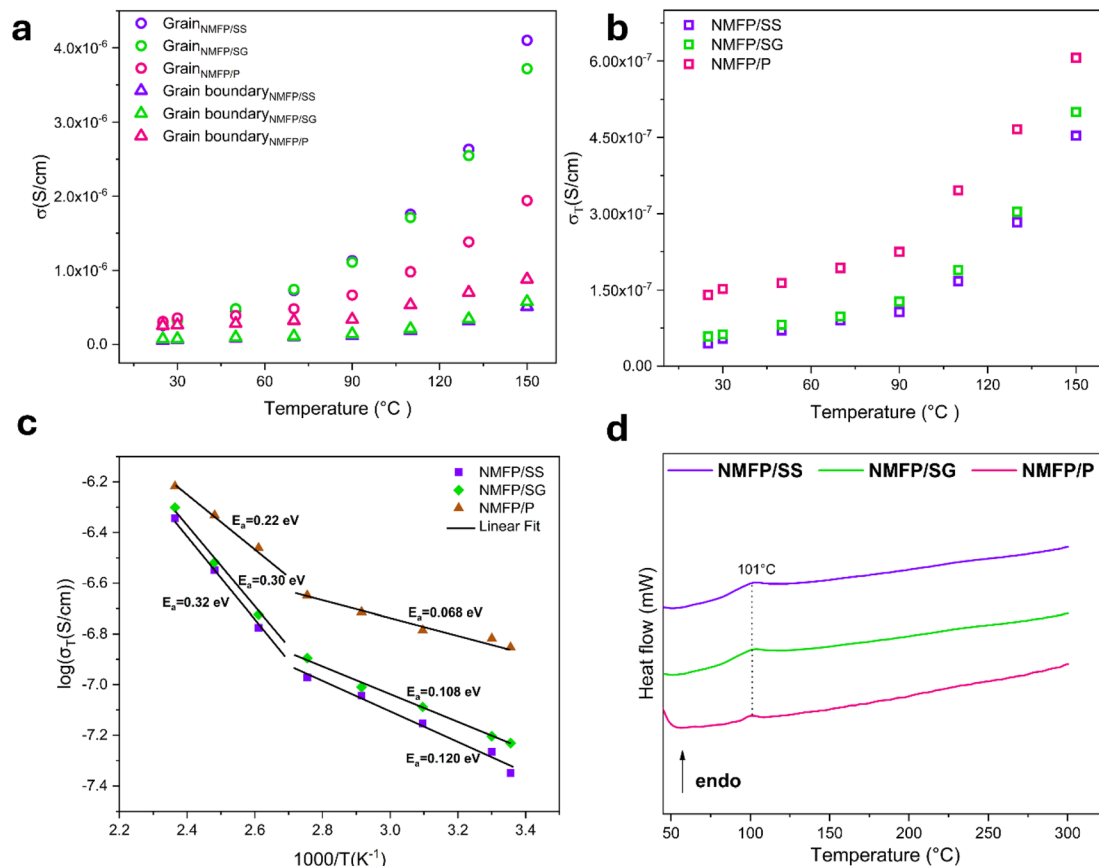


Fig. 5 (a, b) Grain, grain boundary and total conductivities of NMFP pellets as a function of temperature. (c) Arrhenius plots of NMFP pellets. (d) DSC measurement of NMFP samples from 45 to 300 °C.

distinguishable in the case of NMFP/SS and NMFP/SG curves compared with NMFP/P curve. The last region at lower frequency shows a curved spike, describes the sample-electrode interface polarization process. The equivalent sub-circuit that fits the last region is a bit complex, is formed by a resistance ( $R$ ) in series with a Warburg element ( $W_1$ ) and in parallel with a constant phase element (CPE3). The  $R$  resistance corresponds to the metallic electrode resistance. The Warburg element ( $W_1$ ) indicates the presence of blocking diffusion due to the Ag-paste that works as a blocking electrode preventing  $\text{Na}^+$  ions from crossing the interface. The third constant phase element (CPE3) reflects the impedance response arising from the distribution of ionic and electronic polarization processes occurring at the pellet-electrode interface.<sup>39</sup> This equivalent sub-circuit confirms that the conductivity of the materials is a mixture of an ionic and electronic nature.<sup>40</sup> The total equivalent circuit used to fit the impedance spectra is inset in Fig. 4a.

For the three samples, as the temperature increases (Fig. 4b-d), the diameter of the semicircle at high frequency decreases and the incomplete semicircle at intermediate frequency shifts to lower value of  $Z'$ . Additionally, the semicircle at high frequency appears smaller than the incomplete semicircle at lower frequency. These observations indicate the diminution of  $R_G$  and  $R_{GB}$  when the temperature increases, as well as the higher values of  $R_{GB}$  compared to  $R_G$ . The  $R_G$  is estimated from the intercept of the semicircle arc at high frequency on the real impedance axes. The values of  $R_G$  and  $R_{GB}$  were obtained by fitting the impedance data using the equivalent circuit.

The grain, grain boundary and total conductivities of the three samples are calculated using the eqn (1) as shown in Fig. 5a and b. In the temperature range of RT-50 °C, the three samples exhibit nearer grain conductivity values (Fig. 5a), which indicate that the synthesis method is not the main factor governing grain conductivity, but the crystal structure and charge

Table 4 Conductivities of NMFP pellets at 30 °C and the activation energies

Pellets	$\sigma_g$ (S cm <sup>-1</sup> ) $\times 10^{-7}$	$\sigma_{gb}$ (S cm <sup>-1</sup> ) $\times 10^{-7}$	$\sigma_t$ (S cm <sup>-1</sup> ) $\times 10^{-7}$	$E_{aRT \leq T \leq 90^\circ\text{C}}$ (eV)	$E_{a90 < T \leq 150^\circ\text{C}}$ (eV)
NMFP/SS	3.370	0.647	0.543	$0.120 \pm 0.009$	$0.32 \pm 0.02$
NMFP/SG	3.230	0.760	0.626	$0.108 \pm 0.005$	$0.30 \pm 0.03$
NMFP/P	3.590	2.640	1.520	$0.068 \pm 0.006$	$0.22 \pm 0.02$





carrier concentration.<sup>34</sup> As the temperature increases, a noticeable difference is observed between the grain conductivities of the pellets, NMFP/P shows the lower value and NMFP/SS shows the higher value. The lower grain conductivity value of NMFP/P pellets at higher temperature comparing to NMFP/SS and NMFP/SG pellets can be explained by the collision between charge carrier due to their fast kinetic speed.<sup>41</sup> In contrast, the temperature dependence of grain boundary conductivity exhibited consistent trends for the three pellets in the temperature range RT–150 °C (Fig. 5a), which NMFP/P displayed the highest value depending on relative density. At 30 °C as presented in Table 4, grain boundary conductivity of NMFP/P pellet (97.9% relative density) shows value of  $2.64 \times 10^{-7} \text{ S cm}^{-1}$  three times higher than that of NMFP/SG ( $0.760 \times 10^{-7} \text{ S cm}^{-1}$  with  $\approx 93.6\%$  relative density) and four times higher than that of NMFP/SS ( $0.647 \times 10^{-7} \text{ S cm}^{-1}$  with  $\approx 92.3\%$  relative density), revealing a significant correlation between pellet relative density and grain boundary conductivity. The higher density can offer more transfer pathways for charge carriers migration through grain boundaries.<sup>42</sup> The total conductivity (Fig. 5b) of the three pellets follows the same behavior of grain boundary conductivity and shows value of  $0.543 \times 10^{-7}$ ,  $0.626 \times 10^{-7}$  and  $1.520 \times 10^{-7} \text{ S cm}^{-1}$  for NMFP/SS, NMFP/SG and NMFP/P, respectively, at 30 °C (Table 4). In fact, the total conductivity of NMFP/P pellet is significantly higher than that of NMFP/SS and NMFP/SG in all temperature range RT–150 °C. This suggests the predominant role of grain boundary conductivity in governing the total conductivity of our material. It was previously reported that the total conductivity of NASICON material is often governed by the grain boundary conductivity.<sup>43</sup> Therefore, the conductivity of our NASICON samples is significantly affected by the synthesis conditions.

The Arrhenius plot of the total conductivities of the three samples is presented in Fig. 5c. The activation energy of the three samples were calculated using eqn (2). In all cases, two linear regions are present, indicating that each sample is characterized by two activation energies. This behavior can be explained by the presence of a phase transition in the NMFP structure.<sup>44,45</sup> DSC curves of NMFP/SS, NMFP/SG and NMFP/P powders measured between 45–300 °C (Fig. 5d) show the presence of an endothermic weak peak at around 95–102 °C. This peak can be associated with unidentified polymorphic transition. Based on a previous report, R. R. Samigullin *et al.* claimed a temperature-dependence polymorphic transition at 55–65 °C in NASICON  $\text{Na}_4\text{VMn}(\text{PO}_4)_3$ .<sup>46</sup> Consequently, the DSC measurement supports the activation energy behavior, but further temperature-dependent XRD studies are required to reveal more structural information. In the lower temperature region, NMFP/SS, NMFP/SG and NMFP/P samples present activation energies of 0.12, 0.108, 0.068 eV, respectively, associated to the rhombohedral phase. Where, at higher temperatures, all three samples present an activation energy three times higher than that of the first region (Table 4). In both regions, NMFP/P pellets show the lowest activation energy values, *i.e.* 0.068 and 0.22 eV for the first and second regions respectively. Notably, lower than those typically reported in the literature for the NASICON structure.<sup>47</sup> Furthermore, the observed increase in

activation energy at high temperature probably indicated that the remarkable phase transition leads to a phase where  $\text{Na}^+$  ions become minimally mobile because of their order in the structure of the polymorph as in monoclinic NASICON.<sup>47,48</sup>

## 4. Conclusion

In summary,  $\text{Na}_4\text{MnFe}(\text{PO}_4)_3$  NASICON compound with  $R\bar{3}c$  space group was successfully synthesized by solution-assisted solid-state reaction, sol-gel and Pechini methods. The investigation of synthesis-related effects on microstructure and conductivity was reported. The Pechini method led to smaller particle size, resulting in a high-density pellet. The higher density achieved by this method contributes significantly to improving the total conductivity, especially the grain boundary conductivity. Total conductivity value of  $1.52 \times 10^{-7} \text{ S cm}^{-1}$  was obtained for NMFP/P samples at 30 °C with the smaller activation energy of 0.068 eV in the temperature range of RT–90 °C. The lower activation energy obtained at temperatures below 90 °C and lower cost of the precursor materials can make this NASICON phosphate as a promising candidate for future energy storage applications.

## Data availability

The data supporting this article have been included as part of the ESI.†

## Author contributions

Loubna Chayal: data curation, formal analysis, investigation, visualization, writing –original draft. Sirine El Arni: data curation, formal analysis. Mohamed Saadi: supervision, validation, project administration, resources. Abderrazzak Assani: formal analysis, validation. Lahcen Bih: data curation, validation, resources. Jiwei Ma: data curation, validation, resources. Mohammed Hadouchi: data curation, conceptualization, supervision, validation, project administration, resources, writing – review & editing.

## Conflicts of interest

There are no conflicts of interest to declare.

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