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agus riyanto

agus.riyanto@fmipa.unila.ac.id

Universitas Lampung <https://orcid.org/0000-0003-0967-3853>

Ayunis Rizqi Amalia

Universitas Lampung

Ayu Astika

Universitas Lampung

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Sustainable synthesis of $\text{Na}_2\text{FeSiO}_4$ using rice husk-derived silica: effect of calcination temperature on phase formation and electrical properties

Agus Riyanto^a, Ayunis Rizqi Amalia^a, Ayu Astika^a

^aDepartment of Physics, Faculty of Mathematics and Natural Sciences, Universitas Lampung,
Jl. Prof. Soemantri Brojonegoro No. 1, Bandar Lampung, 35145, Indonesia

Corresponding author: agus.riyanto@fmipa.unila.ac.id

Abstract

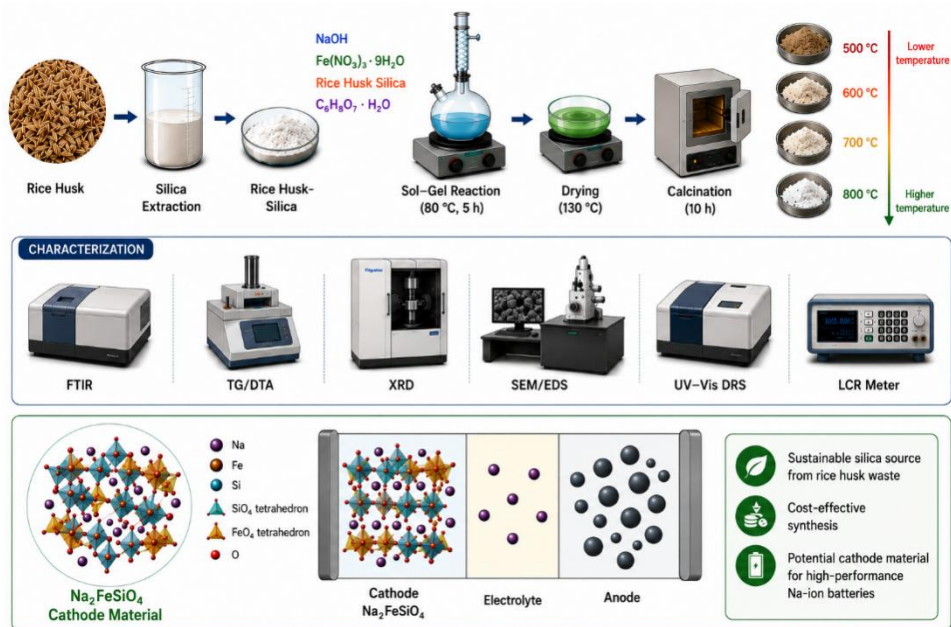
$\text{Na}_2\text{FeSiO}_4$ is a promising cathode material for sodium-ion batteries; however, using conventional silica sources, such as tetraethyl orthosilicate (TEOS), as precursors in its production increases synthesis costs and limits the process's sustainability. This study investigates a waste-derived approach using rice husk-derived silica as an alternative precursor for $\text{Na}_2\text{FeSiO}_4$ synthesis. The effects of calcination temperature on phase formation, morphology, direct optical band gap, and electrical conductivity were systematically evaluated. $\text{Na}_2\text{FeSiO}_4$ was synthesized via a sol-gel method using NaOH, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, rice husk-derived silica, and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ at a molar ratio of 2:1:1:1, followed by calcination at 500 – 800 °C for 10 h. The samples were characterized using FTIR, TG/DTA, XRD, SEM/EDS, UV-Vis DRS, and an LCR meter. $\text{Na}_2\text{FeSiO}_4$ was identified as the dominant phase, with SiO_2 and Na_2SiO_3 as secondary phases. Increasing the calcination temperature enhanced the formation of the $\text{Na}_2\text{FeSiO}_4$ phase, lattice reorganization, and microstructural consolidation, while the direct optical band gap increased from 2.38 to 2.87 eV. Conversely, electrical conductivity decreased with increasing temperature while remaining on the order of 10^{-5} Sm^{-1} , with the highest value observed at 500 °C. These findings demonstrate the potential of rice husk-derived silica as a sustainable and cost-effective precursor for $\text{Na}_2\text{FeSiO}_4$.

Keywords: $\text{Na}_2\text{FeSiO}_4$, phase, electrical conductivity, rice husk-derived silica, waste valorization

Highlights

- $\text{Na}_2\text{FeSiO}_4$ is a promising cathode material for sodium-ion batteries.
- Rice husk waste offers an abundant and low-cost silica source.
- Valorizing rice husk waste promotes sustainable $\text{Na}_2\text{FeSiO}_4$ synthesis.
- Calcination temperature governs the phase and electrical properties of $\text{Na}_2\text{FeSiO}_4$.

Graphical Abstract



29

30 1. Introduction

31 $\text{Na}_2\text{FeSiO}_4$ is a sodium iron orthosilicate composed of silicate polyanionic units together with Fe and Na
 32 cations. Owing to its pronounced structural polymorphism, the crystallographic phase of $\text{Na}_2\text{FeSiO}_4$ is highly
 33 dependent on the synthesis route and processing conditions, leading to multiple polymorphs with distinct
 34 electrochemical properties [1]. Structurally, $\text{Na}_2\text{FeSiO}_4$ consists of a three-dimensional framework constructed from
 35 corner-sharing FeO_4 and SiO_4 tetrahedra, with Na^+ ions occupying interstitial sites within the framework. This
 36 unique structural architecture endows $\text{Na}_2\text{FeSiO}_4$ with excellent structural robustness and the ability to reversibly
 37 accommodate Na^+ ions during electrochemical cycling, making it a promising cathode material for sodium-ion
 38 batteries [2]. Another aspect that promotes the utilization of this material as a cathode is its abundant raw materials,
 39 low toxicity, and high ionic conductivity [3]. The greater distance between atomic layers and the non-directional
 40 bonding between Na^+ and neighboring ions make $\text{Na}_2\text{FeSiO}_4$ exhibit high ionic conductivity [4]. This material is
 41 also known to exhibit sufficiently promising electrical conductivity for cathode applications [5]. Besides, based on
 42 its capacity, the theoretical capacity of $\text{Na}_2\text{FeSiO}_4$ as a cathode material in a rechargeable battery system is 276
 43 mAhg^{-1} [6]. This characteristic certainly contributes to the material's remarkable properties as a battery cathode for
 44 energy storage.

45 Previous studies have employed various synthesis routes and precursor systems to produce $\text{Na}_2\text{FeSiO}_4$.
 46 Among the most widely reported methods are solvothermal [7], solid-state reaction [8], and sol-gel processes [9,
 47 10]. In the solvothermal approach, metastable $\text{Na}_2\text{FeSiO}_4$ was successfully synthesized from $\text{CH}_3\text{COONa} \cdot \text{H}_2\text{O}$,
 48 tetraethyl orthosilicate (TEOS), $\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, and L-ascorbic acid as precursors. However, the resulting product

49 contained secondary phases, including Na_2SiO_3 and Fe_3O_4 , indicating that complete crystallization of the target
50 phase had not been achieved. According to this study, samples treated for 7 days had the highest purity,
51 approximately 85%. From this, it is evident that one obstacle in a solvothermal process is the long reaction time,
52 even though the preparation can be carried out at low temperatures (230 – 300 °C) [7]. Another study reported that
53 highly crystalline, pristine $\text{Na}_2\text{FeSiO}_4$ could be obtained by combustion of a mixture of $\text{Na}_2\text{C}_2\text{O}_4$, FeC_2O_4 , $\text{C}_6\text{H}_{10}\text{O}_4$,
54 and fumed SiO_2 using the conventional solid-state reaction method [8]. However, this route requires relatively long
55 heat treatment at high temperatures (700 °C for 12 hours) under an inert atmosphere. Meanwhile, Ali et al. (2018)
56 reported that high-purity $\text{Na}_2\text{FeSiO}_4$ could be produced from $\text{NaCH}_3\text{COO} \cdot 2\text{H}_2\text{O}$, $\text{FeC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and TEOS via the
57 sol-gel method, followed by thermal treatment at 500 °C for 10 hours. In this study, impurity phases commonly
58 observed in $\text{Na}_2\text{FeSiO}_4$, such as Na_2SiO_3 and Fe_2O_3 , were almost undetectable [11]. Various reported synthesis
59 routes have produced $\text{Na}_2\text{FeSiO}_4$ with relatively high purity; however, each approach still entails inherent trade-
60 offs among reaction kinetics, precursor selection, thermal processing conditions, and the resulting phase purity. This
61 indicates that comprehensive optimization of the synthesis conditions is still required to achieve materials with
62 improved phase purity.

63 Silica is one of the primary precursors in the preparation of $\text{Na}_2\text{FeSiO}_4$, as it provides the silicon source
64 for forming the orthosilicate framework. Several studies have reported that TEOS is widely used as a silica source
65 for producing the material [3, 7, 10, 11]. Nevertheless, the relatively high cost has prompted growing interest in
66 replacing conventional silica precursors with renewable and low-cost alternatives. Among the available biomass
67 resources, rice husk has emerged as a promising silica source owing to its high amorphous silica content, widespread
68 availability, and low economic value. Previous studies report that amorphous silica with a purity above 98% can be
69 recovered from rice husks using a simple, cost-effective extraction process [12, 13]. The extraction mechanism is
70 primarily governed by the pH-dependent solubility of silica. Under strongly alkaline conditions, the Si–O–Si
71 network is progressively dissolved, forming soluble silicate species, whereas silica exhibits negligible solubility
72 under acidic and near-neutral conditions [14]. Subsequent acidification promotes the hydrolysis and condensation
73 of dissolved silicate species, resulting in the precipitation of high-purity amorphous silica [15]. These characteristics
74 make rice husk-derived silica a sustainable and economically attractive alternative to TEOS for the synthesis of
75 $\text{Na}_2\text{FeSiO}_4$ and other silicate-based functional materials.

76 The present study aims to evaluate the feasibility of rice husk-derived silica as a sustainable silica
77 precursor for the synthesis of $\text{Na}_2\text{FeSiO}_4$. In particular, this work systematically investigates the effect of calcination
78 temperature on phase formation and electrical conductivity, which have received little attention. Electrical

properties play a crucial role in the electrochemical performance of $\text{Na}_2\text{FeSiO}_4$; however, they have been relatively underexplored to date. Sufficient electrical properties are required to facilitate charge transport, minimize electrode internal resistance, and enhance charge-transfer processes during electrochemical reactions [16]. Therefore, a systematic investigation of this material's electrical properties is required. The study aims to investigate the phase and electrical properties of the $\text{Na}_2\text{FeSiO}_4$ precursor after thermal treatment, during which nucleation and crystallization are expected to occur. The $\text{Na}_2\text{FeSiO}_4$ precursors were heated to 500 – 800 °C for 10 hours at each peak temperature [16]. The samples were characterized using various techniques, including FTIR for functional group analysis, TG/DTA for thermophysical characterization, XRD for phase analysis, and SEM/EDS for microstructural analysis and element mapping. The electrical properties of the samples were evaluated primarily through electrical conductivity measurements using an LCR meter, with direct optical band gap analysis by UV–Vis DRS serving as complementary supporting evidence.

2. Experimental Methods

2.1. Materials

The raw material used to synthesize $\text{Na}_2\text{FeSiO}_4$ consists of rice husk silica powder prepared from rice husk produced from the rice milling industry in Lampung Province (Indonesia), KOH 90% (Rp Chemical Product), HNO_3 68% (Rp Chemical Product), NaOH 99% (Rp Chemical Product), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 99% (Merck), and chelating agent $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ 100% (Merck).

2.2. Procedure

2.2.1. Silica powder preparation from rice husk

Silica powder was obtained from dried and cleaned rice husks using the alkali extraction method, as reported in a previous study [5]. For extraction, 50 g of rice husk was mixed with 500 mL of 5% KOH solution and heated to a boil for 30 minutes. The mixture was left at room temperature for 24 hours, then filtered through a Millipore filter to separate the solution from the residual rice husk. The solution was acidified by dropwise addition of 10% HNO_3 until it completely gelled. The gel obtained was aged for a day, then repeatedly washed with distilled water to remove the acid. The gel was oven-dried at 100 °C for 2 hours to obtain a solid. The solid was ground and sieved to obtain silica powder with a 200-mesh size.

2.2.2. Preparation of $\text{Na}_2\text{FeSiO}_4$

$\text{Na}_2\text{FeSiO}_4$ was prepared using the sol-gel method, as reported in previous studies [5]. Every sample was made from NaOH, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, rice husk silica powder, and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ with a mole ratio of 2:1:1:1. As much

108 as 0.4 g of NaOH, 2.02 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and 1.05 g of $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ each was dissolved in 10 ml, 25 ml, and
109 20 ml of distilled water, respectively. Meanwhile, 0.3 g of silica was dissolved in an NaOH solution under magnetic
110 stirring at 60 °C for 30 minutes. The solutions of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ were mixed into the silica
111 solution. The mixture was stirred in the reflux system at 80 °C for 5 hours, then poured into a glass beaker. It was
112 stirred at 75 °C to evaporate the solvents, then dried in an oven at 130 °C to obtain a solid. The solid was ground to
113 get a precursor of $\text{Na}_2\text{FeSiO}_4$ powder. The powder was calcined at 500, 600, 700, and 800 °C, with a heating rate
114 of 3 °C/min and a holding time of 10 hours at each peak temperature.

115 2.3. Characterization

116 Functional groups were investigated using a Nicolet iS10 FTIR spectrometer over the spectral range of
117 4000 – 400 cm^{-1} . TG/DTA was performed using an Exstar TG/DTA 7300. The TG/DTA curve was recorded by
118 scanning the $\text{Na}_2\text{FeSiO}_4$ precursor in the temperature range of 30 to 1300 °C. Structural analysis was performed
119 using an X'Pert Powder PW 30/40 diffractometer with Cu-K α radiation ($\lambda = 0.15418 \text{ \AA}$) operated at 40 kV and 30
120 mA. The diffractogram was collected over 10° – 100° in 2 θ with a step size of 0.02°/min. The diffraction patterns
121 of all samples were analyzed using Qual-X software and the Crystallography Open Database (COD) with a search-
122 match method to identify the phases present in each sample. Crystallographic data for the phases present in the
123 sample were used as references for the refinement analysis. The refinement was carried out using Rietica for
124 Windows. Analysis of the microstructure and elemental composition on the surface of the sample was carried out
125 using SEM/EDS Tescan Vega3.

126 The direct optical band gap (E_g) was estimated from diffuse reflectance spectra measured with a
127 Shimadzu UV-2450 UV-Vis spectrophotometer. The direct optical band gap energy was estimated using the
128 Kubelka-Munk function ($F(R) = K/S = (1 - R)^2/2R$), where S and K are the scattering and absorption
129 coefficients, respectively, while R is the diffuse reflectance. The direct optical band gap and the Kubelka-Munk
130 function ($F(R)$) are related through the Tauc relation $[F(R)h\nu]^2 = A(h\nu - E_g)$, where A is the proportionality
131 constant and $h\nu$ is the photon energy. Meanwhile, the electrical conductivity of the $\text{Na}_2\text{FeSiO}_4$ cylinder pellets was
132 measured indirectly using a Hioki 3520-52 over the frequency range of 50 – 60 Hz. The instrument measures
133 electrical conductance (G) as a function of frequency, reflecting the sample's ability to conduct electric current under
134 the applied measurement conditions. The measured conductance values were subsequently converted into electrical
135 conductivity (σ) by taking into account the geometric dimensions of the pellet, namely its thickness (l) and cross-
136 sectional area (A). The electrical conductivity (σ) of each sample was calculated using the $\sigma = Gl/A$ relation.

137 3. Results and discussions

138 3.1. Phase analysis of Na₂FeSiO₄

139 The FTIR spectra recorded over the wavenumber range of 4000 – 400 cm⁻¹ of the precursors calcined at
140 500 – 800 °C are depicted in Fig. 1. As shown in Fig. 1(a), the FTIR spectrum of the calcined sample at 500 °C
141 exhibits a characteristic absorption band located at a range of 910 – 864 cm⁻¹, which is assigned to the stretching
142 vibrations of the Si–O bond of the SiO₄ tetrahedral group [17]. Another prominent absorption band located at 570
143 – 528 cm⁻¹ is attributed to the Fe–O stretching vibration of the FeO₄ tetrahedral [18]. Meanwhile, the absorption
144 peak at 462 cm⁻¹ provides strong evidence for the bending vibration of the Na–O bonds in the NaO₄ tetrahedral [19].
145 The simultaneous presence of these characteristic vibrational modes confirms the formation of the interconnected
146 NaO₄–FeO₄–SiO₄ tetrahedral framework that constitutes the fundamental crystal structure of Na₂FeSiO₄. The
147 spectrum also shows a hydroxyl group (–OH), indicated by a broad band near 3425 cm⁻¹ [11]. The absorption band
148 centered at 3425 cm⁻¹ is assigned to the –OH stretching vibration of adsorbed water molecules and/or surface
149 hydroxyl groups on Na₂FeSiO₄. There are also absorption peaks at 1651 cm⁻¹ and 1458 cm⁻¹. According to a previous
150 study, these two absorption peaks correspond to the stretching vibrations of the C=O and C–H bonds [20]. These
151 residual organic species are attributed to the incomplete decomposition of C₆H₈O₇·H₂O (a chelating agent), as
152 reported before [21].

153 With increasing calcination temperature from 500 to 800 °C, the characteristic absorption bands
154 corresponding to the Si–O, Fe–O, and Na–O vibrations remain clearly observable, indicating that the Na₂FeSiO₄
155 framework is preserved throughout the heat treatment. In contrast, the intensity of the broad –OH absorption band
156 in the region of approximately 3371 – 3286 cm⁻¹ progressively decreases with increasing temperature, reflecting the
157 gradual removal of adsorbed water molecules and surface hydroxyl groups via thermal dehydration [11]. This
158 indicates that an increase in temperature promotes the crystallization process by providing sufficient thermal energy
159 for atomic rearrangement and the formation of a more ordered crystal structure [19].

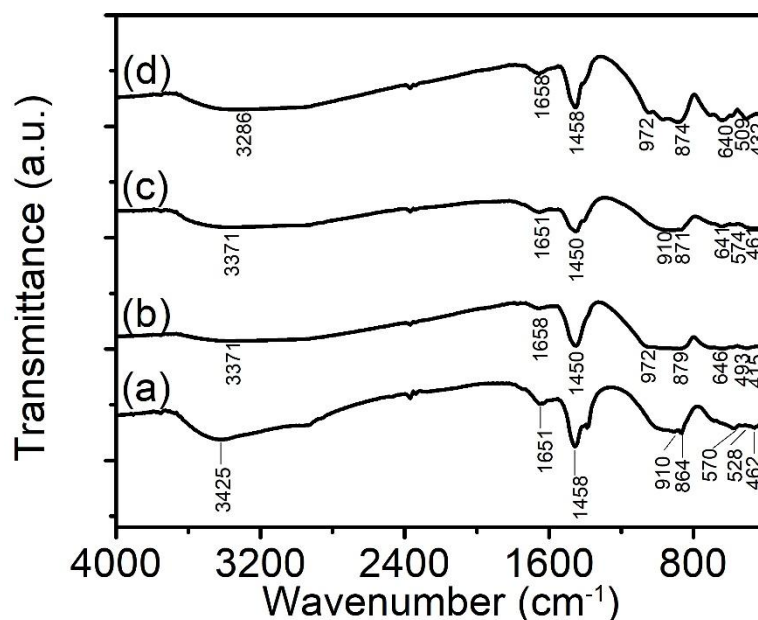


Fig 1. FTIR spectra of $\text{Na}_2\text{FeSiO}_4$ calcined at different temperatures: (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 800 °C.

Fig. 2 presents the simultaneous TG/DTA curves of the $\text{Na}_2\text{FeSiO}_4$ precursor, revealing a sequence of thermally induced transformations occurring during heating. As illustrated in Fig. 2, the DTA profile exhibits two distinct endothermic events within the temperature range of 30 – 271 °C, centered at approximately 104 and 187 °C, which are accompanied by a cumulative mass loss of approximately 43.74% in the corresponding TG curve. These thermal events are attributed to the sequential removal of most of the physically adsorbed moisture, followed by the elimination of more strongly bound hydroxyl species associated with the precursor surface [7, 22]. The next event occurs in the temperature range of 271 – 358 °C and is endothermic, with a peak near 334 °C. This endothermic event is followed by a mass loss of approximately 10.59%. This event is related to the decomposition of citric acid (chelating agent) used to prepare the $\text{Na}_2\text{FeSiO}_4$ precursor [21]. Over the temperature range of 358 – 1300 °C, the DTA curve shows an endothermic peak at 1098 °C, accompanied by approximately 10.44% mass loss. This thermal event indicates a transformation likely associated with the nucleation and crystallization of the $\text{Na}_2\text{FeSiO}_4$ phase [19, 22].

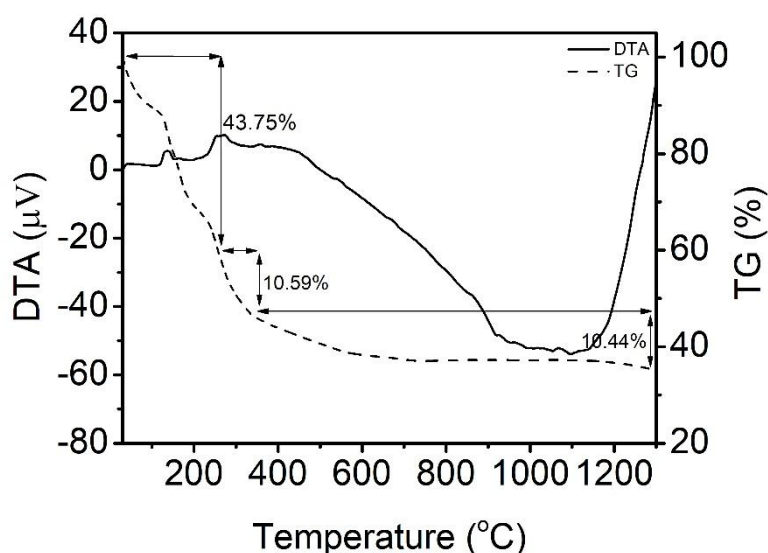
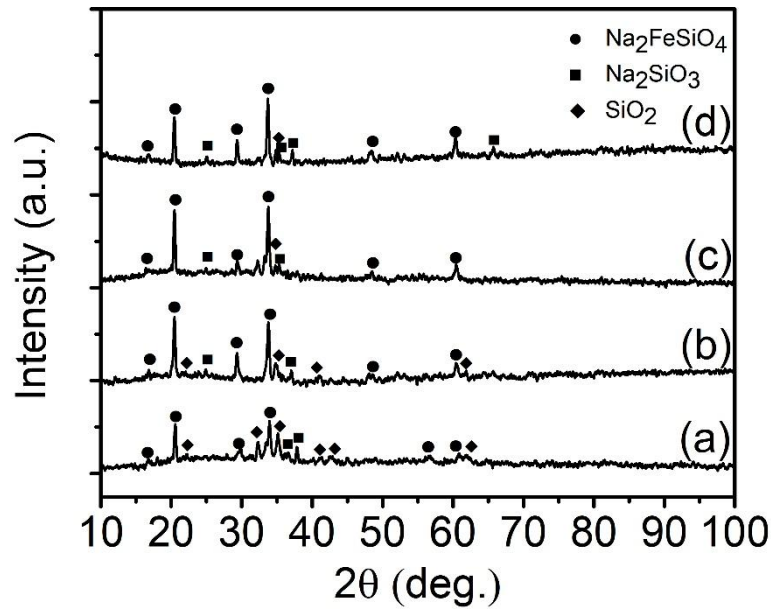


Fig 2. Simultaneous TG/DTA curve of $\text{Na}_2\text{FeSiO}_4$ precursor.

The phase formation of samples was characterized using XRD. The phases present in the sample were identified by comparing the sample's diffraction pattern with diffraction lines from the COD using the QualX program via the search-match method. Since a dedicated crystallographic entry for $\text{Na}_2\text{FeSiO}_4$ is currently unavailable in the COD database, phase assignment was carried out using structurally analogous orthosilicate compounds. This approach is well established for $\text{Na}_2\text{FeSiO}_4$ because it crystallizes in a tetrahedral orthosilicate framework that is isostructural with several orthosilicates, including $\text{Na}_2\text{CaSiO}_4$, $\text{Na}_2\text{ZnSiO}_4$, and $\text{Na}_2\text{MnSiO}_4$, all of which exhibit closely related atomic arrangements and diffraction characteristics. Consequently, the use of isostructural reference compounds provides a reliable basis for phase identification when direct crystallographic data are unavailable [7, 11]. The search-match results showed that the diffraction patterns closely matched those of the $\text{Na}_2\text{CaSiO}_4$ crystallographic database (COD 00-101-0111). Besides, the results of the search-match method indicated the presence of secondary phases marked by the presence of diffraction peaks associated with the Na_2SiO_3 phase (COD 00-231-08580) and SiO_2 (COD 00-900-0520). Based on this method, the sample is identified as containing the $\text{Na}_2\text{FeSiO}_4$ phase with a cubic crystal structure and space group P 21 3, consistent with a previous study [23]. Meanwhile, the Na_2SiO_3 phase has an orthorhombic structure with a space group of C M C 21, and the SiO_2 phase has a monoclinic structure with a space group of C 1 C 1. The diffraction peaks associated with the three phases are shown in the X-ray diffractogram in Fig. 3. The corresponding peaks indicate that $\text{Na}_2\text{FeSiO}_4$ is the predominant crystalline phase in all samples, accompanied by minor SiO_2 and Na_2SiO_3 secondary phases. The persistence of these secondary phases has also been reported in previous studies, indicating that complete conversion of the precursor into $\text{Na}_2\text{FeSiO}_4$ remains challenging during synthesis [7, 24]. With increasing calcination

196 temperature, the characteristic diffraction peaks of $\text{Na}_2\text{FeSiO}_4$ become progressively sharper and more pronounced,
 197 indicating enhanced phase formation, crystallinity, and crystallite development.



198

199 Fig 3. XRD diffractogram of $\text{Na}_2\text{FeSiO}_4$ calcined at different temperatures: (a) 500 °C, (b) 600 °C, (c) 700 °C,
 200 and (d) 800 °C.

201

202 To obtain a more comprehensive understanding of the phase formation and lattice parameters in the
 203 synthesized powders, the experimental XRD patterns were refined using crystallographic information. The
 204 representative refined diffraction patterns are presented in Fig. 4, while the corresponding figures of merit are
 205 summarized in Table 1. The calculated profiles show good agreement with the experimental patterns, as indicated
 206 by the relatively low residual factors and satisfactory goodness-of-fit (GoF) values, confirming that the adopted
 207 crystallographic models adequately reproduce the observed diffraction features [25]. The refinement results were
 208 subsequently used to determine the lattice parameters of each phase, thereby allowing evaluation of the thermally
 209 induced changes in the crystal lattice. The systematic changes in the refined lattice parameters (in Table 2) further
 210 suggest thermally induced lattice reorganization during the formation and crystallization of $\text{Na}_2\text{FeSiO}_4$. The
 211 progressive lattice contraction observed in the $\text{Na}_2\text{FeSiO}_4$ and SiO_2 phases can be attributed to thermally induced
 212 atomic rearrangement and to the reduction of structural imperfections generated during synthesis. As the calcination
 213 temperature increases, enhanced atomic diffusion facilitates the redistribution of constituent ions to more
 214 energetically favorable crystallographic sites, thereby improving structural ordering and crystallinity. Consequently,
 215 the crystal framework becomes more compact and densely packed, as reflected by the reduction in the unit-cell
 dimensions [21].

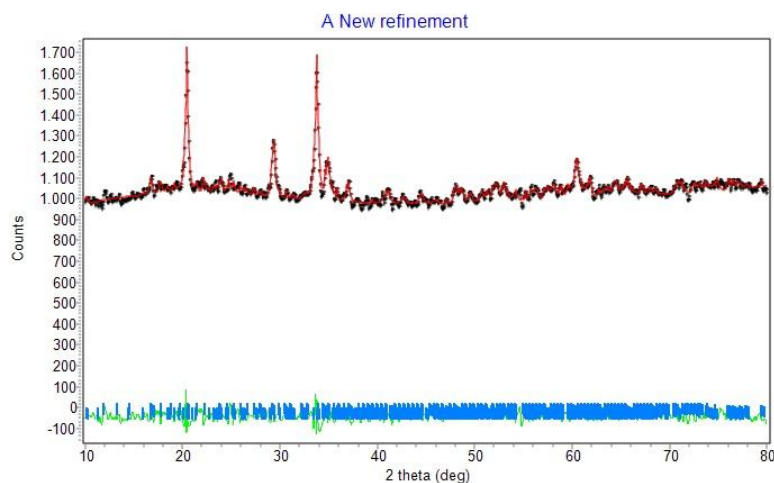


Fig 4. Representative XRD refinement plot of $\text{Na}_2\text{FeSiO}_4$.

Table 1. Figure of merit from refinement of XRD data of $\text{Na}_2\text{FeSiO}_4$ calcined at different temperatures.

$\text{Na}_2\text{FeSiO}_4$ calcined at	R_{exp}	R_{wp}	R_{p}	GoF
500 °C	2.52	1.57	1.00	0.39
600 °C	2.73	1.80	1.15	0.43
700 °C	2.48	1.73	1.02	0.48
800 °C	3.18	2.18	1.43	0.47

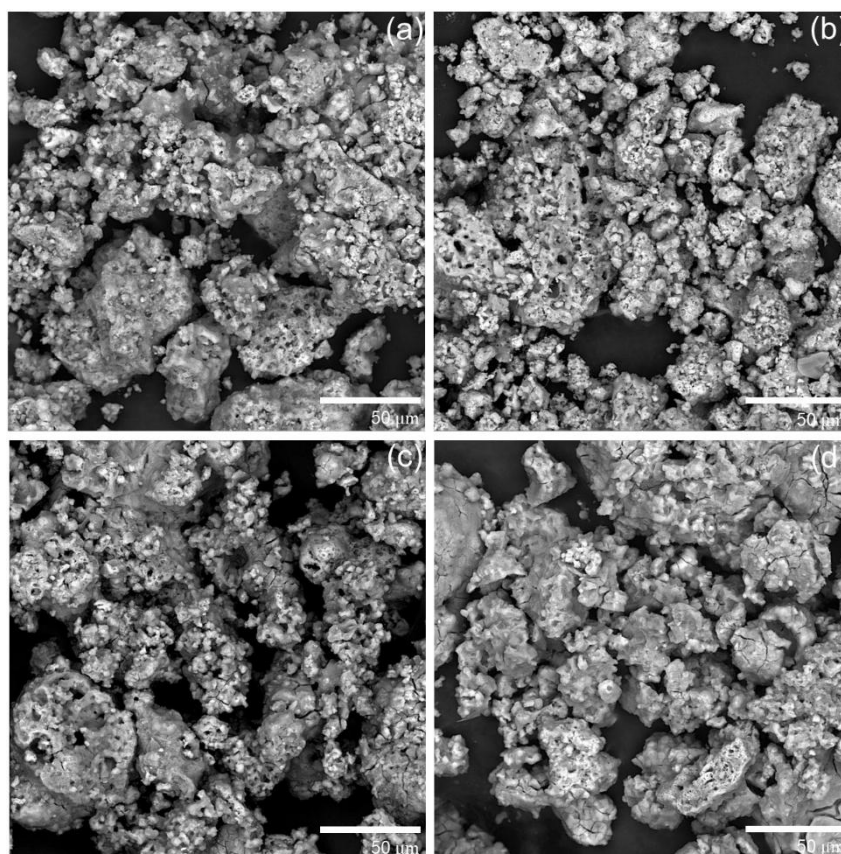
Table 2. Lattice parameters of multiple phases obtained from refinement.

$\text{Na}_2\text{FeSiO}_4$ calcined at (°C)	Lattice parameter of $\text{Na}_2\text{FeSiO}_4$				Lattice parameter of Na_2SiO_3				Lattice parameter of SiO_2					
	a (Å)	b (Å)	c (Å)	$\alpha = \beta = \gamma$ (°)	a (Å)	b (Å)	c (Å)	$\alpha = \beta = \gamma$ (°)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
500	14.980	14.980	14.980	90.000	10.000	6.070	48.200	90.000	18.087	5.000	23.040	90.000	105.800	90.000
600	14.950	14.950	14.950	90.000	10.000	6.070	48.200	90.000	17.880	5.000	22.920	90.000	104.050	90.000
700	14.502	14.502	14.502	90.000	10.000	6.070	48.200	90.000	13.000	5.000	16.300	90.000	105.982	90.000
800	14.400	14.400	14.400	90.000	10.000	6.070	48.200	90.000	9.999	5.000	13.000	90.000	109.820	90.000

These structural changes are consistent with the thermal behavior observed in the TG/DTA analysis (Fig. 2), where the thermal events within the relevant temperature range indicate processes associated with the nucleation and crystallization of the target phase. Increasing the calcination temperature provides sufficient thermal energy to promote atomic diffusion and the rearrangement of constituent species toward the formation of the $\text{Na}_2\text{FeSiO}_4$ crystal framework. The FTIR results further support this interpretation through the progressive attenuation of hydroxyl-related absorption bands, indicating the removal of residual hydroxyl species and adsorbed water during thermal treatment [21]. Collectively, the TG/DTA, FTIR, XRD, and refinement results demonstrate that increasing calcination temperature promotes crystallization and structural ordering of $\text{Na}_2\text{FeSiO}_4$. Furthermore, the successful formation of crystalline $\text{Na}_2\text{FeSiO}_4$ from rice husk-derived silica demonstrates the suitability of this agricultural waste as a precursor for the synthesis of $\text{Na}_2\text{FeSiO}_4$. The formation of the target phase through the employed sol–gel route indicates that the extracted silica possesses sufficient chemical reactivity to participate in the formation of

231 the $\text{Na}_2\text{FeSiO}_4$ framework. Thus, rice husk-derived silica represents a promising, sustainable alternative to
232 conventional silica sources, offering an effective pathway to valorize agricultural waste into functional sodium iron
233 silicate materials.

234 The morphological characteristics of the synthesized powders are shown in the SEM micrographs in Fig.
235 5. The sample calcined at 500 °C exhibits irregularly shaped, loosely packed micrometer-sized grains with
236 relatively rough surfaces and numerous cavities, indicating a porous microstructure (Fig. 5a) [8, 16]. With
237 increasing calcination temperature to 600 and 700 °C, the irregular morphology is retained, although surface
238 cavities become more apparent (Fig. 5b–c). At 800 °C, the particles appear relatively more compact, accompanied
239 by a reduction in surface cavities (Fig. 5d). These morphological changes are consistent with the progressive
240 crystallization and structural consolidation indicated by the TG/DTA and XRD analyses. The increased thermal
241 energy promotes atomic diffusion and rearrangement, thereby facilitating crystallization and improving
242 interparticle contact, while producing only limited changes in the overall particle morphology.



243
244 Fig 5. SEM images of $\text{Na}_2\text{FeSiO}_4$ calcined at different temperatures: (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d)
245 800 °C.

The elemental composition and spatial distribution of the synthesized powders were further investigated using EDS. The representative EDS results are presented as elemental maps shown in Fig. 6(a). The elemental maps reveal the spatial distributions of O, Na, Fe, and Si across the analyzed regions depicted in Fig. 6(b – d), while the corresponding EDS spectrum provides the characteristic X-ray signals for these elements, as shown in Fig. 6(f). All four constituent elements are detected in the samples, with relatively homogeneous spatial distributions throughout the analyzed areas. The elemental compositions are relatively similar across the samples (Table 3), indicating that calcination primarily affects crystallinity and microstructural characteristics rather than substantially altering the overall elemental composition. The coexistence of Na, Fe, Si, and O is consistent with the elemental constituents of the $\text{Na}_2\text{FeSiO}_4$ -based material, while the phase composition and the presence of secondary phases are established from the XRD analysis.

Table 3. Atomic composition on the surface of the samples.

$\text{Na}_2\text{FeSiO}_4$ calcined at	Atom (%)			
	Oxygen (O)	Sodium (Na)	Iron (Fe)	Silicon (Si)
500 °C	51.97	30.56	11.15	6.38
600 °C	50.04	29.87	13.88	6.21
700 °C	48.64	33.81	11.66	5.89
800 °C	51.12	32.21	11.01	5.66

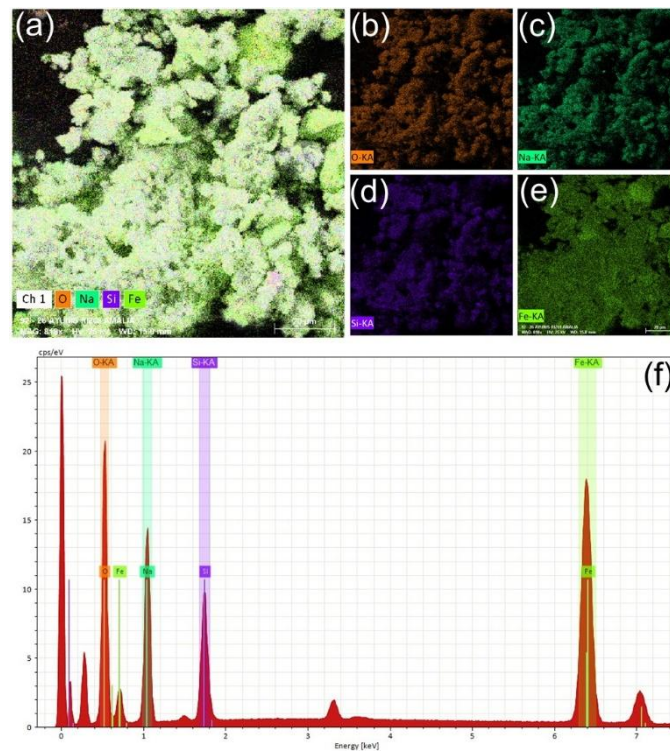


Fig 6. (a) Representative elemental mapping, (b) O, (c) Na, (d) Si, (e) Fe, and (f) the EDS spectrum of $\text{Na}_2\text{FeSiO}_4$.

3.2 Electrical properties

The electrical characteristics of the $\text{Na}_2\text{FeSiO}_4$ samples were initially investigated by examining their electronic structure, with particular emphasis on the direct optical band gap. It was determined using Tauc plot analysis of the diffuse reflectance spectra to elucidate the electronic transitions at the material's absorption edge. This electronic characterization subsequently provides a basis for interpreting the material's charge-transport characteristics. Meanwhile, the electrical conductivity was independently evaluated to assess the influence of calcination-induced structural changes on charge transport. This approach enables a comprehensive assessment of the correlations among the development of the crystal structure, the direct optical band gap, and the electrical characteristics of $\text{Na}_2\text{FeSiO}_4$.

The Tauc plots in Fig. 7 exhibit well-defined linear regions near the absorption edge for all samples, enabling the optical band gap to be estimated by extrapolating the linear portions to their intersection with the photon-energy axis. The direct optical band gap increases systematically from 2.38 eV for the sample calcined at 500 °C to 2.67, 2.78, and 2.87 eV for the samples calcined at 600, 700, and 800 °C, respectively. The value obtained at 800 °C is comparable to the theoretically reported band gap of approximately 2.83 eV for carbon-coated $\text{Na}_2\text{FeSiO}_4$ [24]. The progressive increase in the direct optical band gap indicates that thermal treatment modifies the electronic structure of $\text{Na}_2\text{FeSiO}_4$ concomitantly with its structural growth. The difference in the direct optical band gap is consistent with the structural changes identified by XRD and with the FTIR and SEM/EDS analyses. Increasing the calcination temperature promotes crystallization and enhances structural ordering, accompanied by systematic changes in the lattice parameters (Table 2). The resulting lattice contraction reflects thermally induced atomic rearrangement toward a more compact crystalline framework. Such structural reorganization can modify the local coordination environment and interatomic interactions, thereby influencing the electronic states near the valence- and conduction-band edges [26]. Accordingly, the increase in the direct optical band gap should be attributed to the progressive development of the crystalline framework rather than solely to the contraction of the lattice parameters. This optical response provides further evidence that calcination not only alters the long-range structural ordering but also modulates the electronic characteristics of $\text{Na}_2\text{FeSiO}_4$.

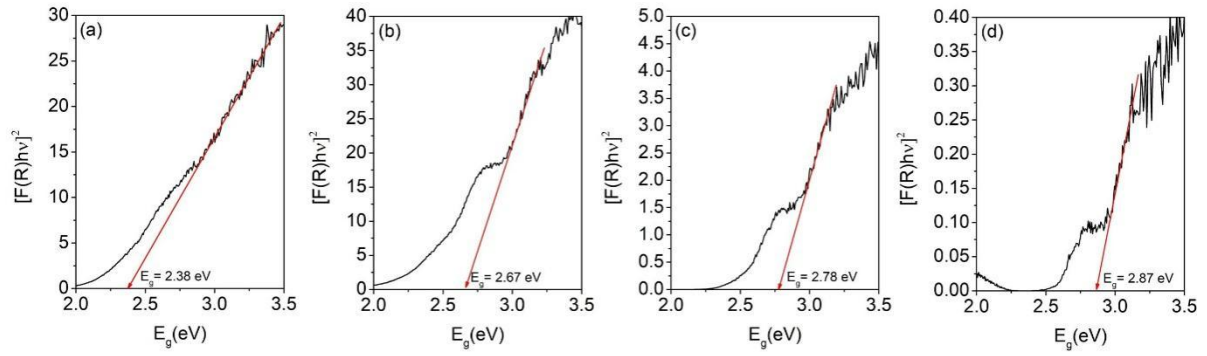


Fig 7. Direct optical band gap of $\text{Na}_2\text{FeSiO}_4$ calcined at different temperatures: (a) 500 °C, (b) 600 °C, (c) 700 °C, and (d) 800 °C.

The electrical conductivity measured over the frequency range of 50 – 60 Hz is presented in Fig. 8, while the corresponding conductivity ranges are summarized in Table 4. The results show that the electrical conductivity of all samples is on the order of 10^{-5} Sm^{-1} and decreases progressively as calcination temperature increases. The highest conductivity is observed for the sample calcined at 500 °C, whereas the lowest value is obtained for the sample calcined at 800 °C. This trend occurs concurrently with an increase in the direct optical band gap, suggesting that thermally induced modifications in the electronic structure may contribute to the reduction in charge transport. A larger direct optical band gap generally implies a higher energy requirement for electronic excitation and may consequently reduce the availability of thermally activated electronic charge carriers. An inverse relationship between band gap and electrical conductivity has also been reported for semiconductor materials [27].

Nevertheless, the optical band gap should not be regarded as a direct determinant of electrical conductivity, because charge transport is also governed by carrier concentration, structural imperfections, secondary phases, and microstructural characteristics. The relatively high conductivity of the 500 °C sample, despite its lower degree of crystallization, is therefore particularly noteworthy. At this temperature, the material exhibits the lowest optical band gap and a relatively expanded lattice compared with the samples treated at higher temperatures. In addition, the incompletely crystallized structure is likely to retain a higher concentration of structural imperfections and local disorder. Such structural characteristics may generate localized electronic states and influence charge-carrier transport. The presence of SiO_2 and Na_2SiO_3 as secondary phases may also affect the measured electrical response by influencing grain boundaries and interfacial regions. The relatively high electrical conductivity of the sample calcined at 500 °C may also be attributed to its distinctive microstructural characteristics, including irregular grains, a relatively rough surface, and a loosely packed particle arrangement.

These features indicate that the material remains at an early stage of crystallization and has not yet undergone substantial structural consolidation, thereby retaining a relatively high density of local disorder and structural defects. Such imperfections can introduce localized electronic states that may contribute to charge-carrier transport. In this regard, the electrical response at 500 °C is likely governed by a combination of a relatively narrow optical band gap, defect-associated electronic states, and a less consolidated microstructure, rather than by crystallinity alone [16].

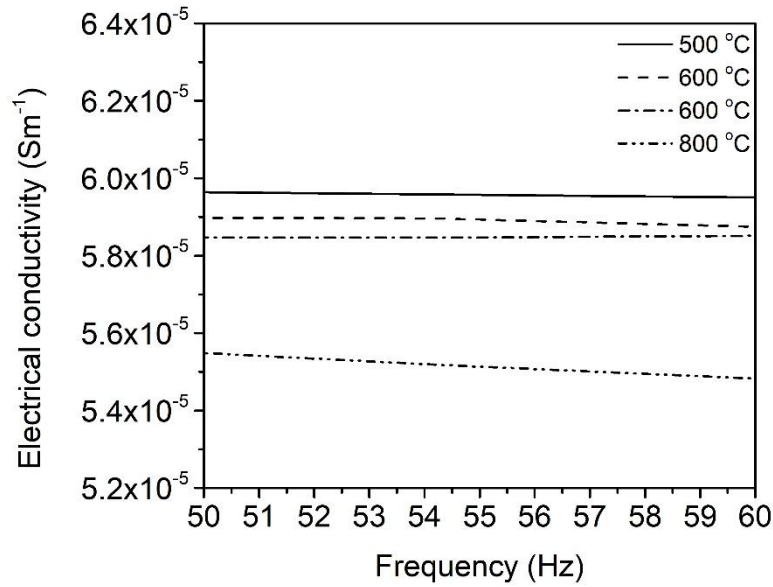


Fig 8. Electrical conductivity of Na₂FeSiO₄ calcined at different temperatures.

With increasing calcination temperature, the structural and electronic characteristics progressively evolve toward a more ordered crystalline state. Although this structural consolidation promotes the development of the crystalline Na₂FeSiO₄ phase, it is simultaneously accompanied by an increase in the optical band gap and a decrease in electrical conductivity. This behavior indicates that enhanced crystallinity does not necessarily improve charge transport in Na₂FeSiO₄. Instead, the electrical response results from a balance between structural ordering and microstructural characteristics that can either facilitate or impede charge-carrier transport. Increased crystallinity may reduce the concentration of defect-related localized states that contribute to carrier transport, while the accompanying microstructural consolidation and grain development can alter the pathways available for charge migration. Therefore, optimizing the calcination temperature should consider not only the formation and development of the crystalline Na₂FeSiO₄ phase but also the structural and electronic factors that govern its electrical response [5, 28]. For the investigated system, calcination at 500 °C produces the highest electrical

conductivity, whereas further increases in calcination temperature promote greater structural ordering, a wider direct optical band gap, and consequently lower electrical conductivity.

Table 4. Electrical conductivity of Na₂FeSiO₄ calcined at different temperatures.

Na ₂ FeSiO ₄ calcined at (°C)	Electrical conductivity ($\times 10^{-5}$) (Sm ⁻¹)
500	5.95 – 5.96
600	5.88 – 5.89
700	5.84 – 5.85
800	5.49 – 5.54

4. Conclusions

This study demonstrates that rice husk can be valorized as an alternative silica source for the synthesis of Na₂FeSiO₄ via a sol–gel route, offering a more sustainable pathway than conventional silica precursors. Na₂FeSiO₄ was successfully formed as the dominant phase across all calcination temperatures, while increasing the temperature from 500 to 800 °C led to enhanced formation of the Na₂FeSiO₄ phase, lattice reorganization, and microstructural consolidation. These structural changes were accompanied by an increase in the direct optical band gap from 2.38 to 2.87 eV and a decrease in electrical conductivity, which remained on the order of 10⁻⁵ Sm⁻¹. The highest conductivity observed at 500 °C indicates that the electrical response is governed by the combined effects of crystal structure, secondary phases, and microstructure. Overall, these findings demonstrate that rice husk can not only replace conventional silica sources with an abundant, low-value, waste-derived feedstock but also enable the production of Na₂FeSiO₄ with tunable structural and electrical characteristics through thermal treatment. This strategy provides a promising approach for integrating agricultural waste valorization into the development of functional materials for more sustainable battery technologies.

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Declarations

Competing interests

The authors have no relevant financial or non-financial interests to disclose.

Data Availability

353 The datasets generated during and/or analyzed during the current study are available from the corresponding author
354 on reasonable request.

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