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# New promising NASICON material as solid electrolyte for sodium-ion batteries: Correlation between composition, crystal structure and ionic conductivity of $Na_{3+x}Sc_2Si_xP_{3-x}O_{12}$

M. Guin [a,*], F. Tietz [a,b], O. Guillon [a,b,c]

[a] Forschungszentrum Jülich GmbH, Institute of Energy and Climate Research (IEK-1): Materials Synthesis and Processing, D-52425 Jülich, Germany
[b] Helmholtz-Institute Münster, c/o Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany
[c] Jülich Aachen Research Alliance, JARA-Energy, Germany

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ABSTRACT

In the search for novel sodium-ion conductors to be used in batteries for grid application, the thoroughly studied class of NASICON materials is of great interest due to compositional diversity and high ionic conductivity. The solid solution $Na_{3+x}Sc_2(SiO_4)_x(PO_4)_{3-x}$ with $0.05 \le x \le 0.8$ was investigated for the first time. The various compositions were synthesized by solid state reaction and their crystallographic and electrical properties were measured. As a result, one of the best sodium-conductive NASICON materials to date was obtained for $x = 0.4$ ($\sigma_{Na,Total} = 6.9 \times 10^{-4}$ S cm$^{-1}$ at 25 °C). Furthermore, the importance of the sodium concentration and size of lattice parameters on the ionic conductivity were investigated. The bulk ionic conductivity was correlated with the structural parameters along the conduction pathway of the sodium ions and confirm the key influence of the interatomic Na–O distances on sodium ion transport.



## 1. Introduction

In 1976, Hong et al. introduced the term NASICON [1,2] to describe the very high ionic conductivity in $Na_3Zr_2Si_2PO_{12}$. This term is now used for all ceramic materials with the same crystal structure and the general composition $A_{1+2x+y+z}M^{(II)}_xM^{(III)}_yM^{(IV)}_{2-x-y}Si_zP_{3-z}O_{12}$ where A is usually a mono- or divalent cation (here, A = Na) and M are divalent, trivalent or tetravalent cations; P can also be substituted with Si or As. The materials belonging to the NASICON family are very attractive because of their compositional diversity leading to many possible applications, such as electrode materials or solid electrolytes in batteries as tested in an all-NASICON battery by Lalère et al. [3], $Cl_2$ and $CO_2$ sensors [4,5], or photoluminescent devices [6]. The conductivity of the NASICON materials is strongly related to their Na concentration and their crystallographic structure, which is influenced by the size of the M cations. It has been concluded from a literature survey [7] that the average ionic radius of M cations should be close to the ionic radius of Zr, i.e. $r_{Zr} = 0.72$ Å [8], in order to obtain highly conductive materials comparable to β- and β″-alumina [9,10]. In addition, the NASICON materials with the highest sodium ion conductivity contain 3–3.5 mol Na per formula unit and show a monoclinic distortion of the crystallographic lattice [7].

Following these guidelines for designing sodium ion conductors, the new solid solution $Na_{3+x}Sc_2Si_xP_{3-x}O_{12}$ (abbreviated hereafter as $NSSiP_x$) was investigated. The ionic radius of Sc of 0.745 Å [8] is close to the ionic radius of Zr and the presence of the trivalent Sc leads to a high amount of Na per formula unit. The introduction of Si in the highly conductive $Na_3Sc_2(PO_4)_3$ ($2.3 \times 10^{-5}$ S cm$^{-1}$ at room temperature) [11] was inspired by the work of Hong on $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ [1] and of Vogel et al. on $Na_{1+x}Hf_2Si_xP_{3-x}O_{12}$ [12]. In both cases, the substitution with Si in the structure led to a significant increase in conductivity. Different structural parameters were correlated with the measured ionic conductivity in order to better understand the impact of Si substitution on the $Na^+$ transport in the scandium-based NASICON materials.

## 2. Experimental

All compositions were synthesized via conventional solid state reaction. A stoichiometric homogenized mixture of $NH_4H_2PO_4$ (Merck KGaA, 99%), $Sc_2O_3$ (Projector GmbH, 99.5%), $Na_2CO_3$ (Alfa Aesar GmbH & Co KG, 99.5%), and $SiO_2$ (Alfa Aesar GmbH & Co KG, 99.8%) was heated with 300 K h$^{-1}$ to 900 °C for 4 h. After grinding, the powder was again annealed for 20 h between 1280 °C and 1350 °C depending on the composition [11,13–15]. The obtained powder was milled and pressed into pellets (13 mm in diameter, approximately 2–5 mm height) and sintered at the annealing temperature of the powder for 10 h.

* Corresponding author.
*E-mail address:* m.guin@fz-juelich.de (M. Guin).

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The purity of the samples was controlled by X-ray diffraction (XRD) measurements (Bruker D4 ENDEAVOR diffractometer, Cu $K_\alpha$ radiation). The powder patterns were analyzed by Rietveld refinements using the Jana program [16] to determine lattice parameters, atomic positions and site occupancies.

The stoichiometry of the materials was controlled by inductively coupled plasma optical emission spectroscopy (ICP-OES) using the Thermo Scientific iCAP7600 spectrometer with optical scale and CID semi-conductor detector, axial und radial reflection, and wavelengths between 166 nm and 847 nm. 10 g of powder were mixed to 0.25 g lithium borate in a platinum crucible and heated for 0.5 h at 1000 °C. The liquefied material was dissolved in 30 mL HCl (5%) and filled to 50 mL volume.

Gold electrodes were sputtered on the surfaces of the pellets for conductivity measurements and the samples were put into Swagelok cells in an Ar-filled glovebox. The ionic conductivity from −30 to 30 °C was determined from impedance spectroscopy data measured with a multi-potentiostat VMP-300 from Bio-Logic SAS, France. The frequency range used was 1 Hz–7 MHz at intervals of 20 points per decade with an amplitude of 100 mV. The ionic conductivity from 30 to 400 °C was measured in argon (ProGasMix from NorECs) with the Alpha-A high performance modular measurement system (Novocontrol Technologies).

## 3. Results and discussion

### 3.1. Crystal structure

$NSSiP_x$ was synthesized in the compositional range of $0.05 \le x \le 0.8$. For $x \ge 0.1$, $NSSiP_x$ crystallizes with rhombohedral structure at room temperature (Fig. 1a). $NSSiP_{0.05}$ is a mixture of rhombohedral and monoclinic phases as shown in Fig. 1b, in which the XRD patterns of the samples $NSSiP_{0.05}$ and $NSSiP_{0.1}$ are enlarged for the diffraction angles between 18° and 30°. The appearance of three reflections at $2\theta = 19.5°$ and two reflections at $2\theta = 28°$ are characteristic for the presence of the monoclinic phase in the powder [17].

The stoichiometry of the $NSSiP_x$ compounds determined by ICP-OES is summarized in Table 1. The semi-quantitative results were normalized to 2 mol Sc/formula unit.

**Table 1**
Composition of the $NSSiP_x$ compounds determined by ICP-OES (experimental errors in the last digits are given in brackets).

| Compound | Composition determined by ICP-OES |
|---|---|
| $NSSiP_{0.1}$ | $Na_{2.90(2)}Sc_2Si_{0.109(8)}P_{2.90(2)}O_{11.9}$ |
| $NSSiP_{0.2}$ | $Na_{2.99(5)}Sc_2Si_{0.219(6)}P_{2.90(7)}O_{12.2}$ |
| $NSSiP_{0.3}$ | $Na_{3.02(7)}Sc_2Si_{0.291(8)}P_{2.71(8)}O_{11.9}$ |
| $NSSiP_{0.4}$ | $Na_{3.12(6)}Sc_2Si_{0.388(9)}P_{2.58(5)}O_{11.8}$ |
| $NSSiP_{0.5}$ | $Na_{3.34(8)}Sc_2Si_{0.49(1)}P_{2.46(5)}O_{11.8}$ |
| $NSSiP_{0.6}$ | $Na_{3.40(8)}Sc_2Si_{0.60(1)}P_{2.43(5)}O_{12.0}$ |
| $NSSiP_{0.8}$ | $Na_{3.51(8)}Sc_2Si_{0.80(2)}P_{2.16(5)}O_{11.8}$ |

It is noticeable that the amount of Na per formula unit was lower than expected for all the compounds. This is due to small weight losses during synthesis caused by the evaporation of sodium at temperatures above 1200 °C. The amount of oxygen per formula unit was not determined experimentally but calculated to compensate the charges.

The Rietveld refinements of all the compositions from Table 1 were carried out for $10° \le 2\theta \le 140°$ with full-matrix least-square against $F^2$ [18]. The starting parameters of the crystal structure were taken from the rhombohedral high-temperature structure of $Na_3Sc_2(PO_4)_3$ described by Boilot et al. [17] and the Pseudo-Voigt profile function was used. All atomic positions, lattice parameters and thermal displacement parameters could be refined for Sc, P/Si and O. Full site occupancy was fixed for the Sc and O positions and the site occupancy of P/Si was adapted to the stoichiometry.

After refinement of the framework atoms, the occupancy of the atomic positions Na(1) and Na(2) (*6b* and *18e*, respectively) was refined but the obtained Na concentration in the structure model was lower than the Na content determined by ICP-OES. Trying to fix the occupancy at higher values resulted in thermal displacement parameters with negative electron density for at least one of the Na atomic positions. Therefore a third Wyckoff position for Na was introduced in analogy to the structure refinements of $Na_{3.35}Zr_2Si_{2.35}P_{0.65}O_{12}$ [19], corresponding to a displacement of the Na(2) position due to the high mobility of the Na ions in the materials at room temperature. The $R_p$ value then decreased from 12–10% to 7–5% depending on the composition. No other possible Na position could be found.

The ratio of the occupancy of the Na(1), Na(2) and Na(3) positions was fixed as a starting value [19] and adapted to the stoichiometry

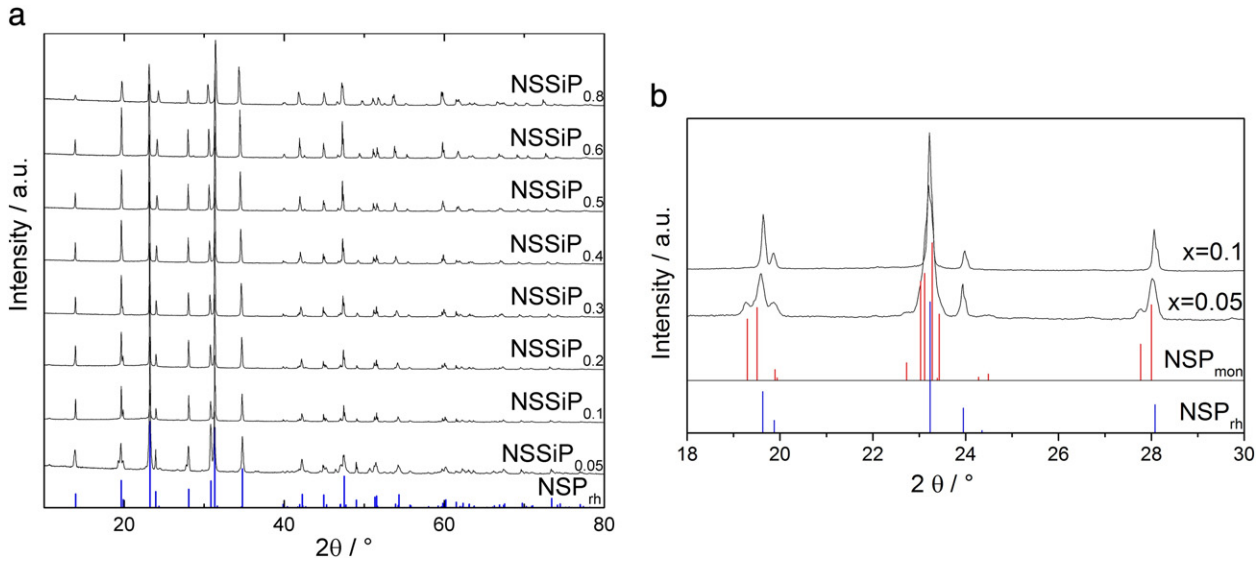


**Fig. 1.** (a) XRD patterns of $NSSiP_x$ for $0.05 \le x \le 0.8$. (b) Detail of the XRD patterns of $NSSiP_{0.05}$ and $NSSiP_{0.1}$ between $2\theta = 18°$ and 30° and comparison with the XRD patterns of rhombohedral ($NSP_{rh}$) and monoclinic ($NSP_{mon}$) $Na_3Sc_2(PO_4)_3$ [17].