Investigation of crystal structure and ionic transport in a scandium-based NASICON material by neutron powder diffraction

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Abstract

A study of the series $\text{Na}_{3+x}\text{Sc}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ($0 < x < 0.8$) revealed very high ionic conductivity values at room temperature. The structural investigation of the substitutional disorder and position of the very mobile Na^+ ions in the crystal structure is the key to understanding the structure-property-chemical bonding relationships. Therefore neutron powder diffraction was carried out at 300 and 100 K on $\text{Na}_{3.4}\text{Sc}_2\text{Si}_{0.4}\text{P}_{2.6}\text{O}_{12}$ to refine the structural parameters and to elucidate the Na^+ distribution in the crystal structure.

The refinement of the structure revealed that two phases are present, one rhombohedral Si-rich phase and one monoclinic $\text{Na}_3\text{Sc}_2\text{P}_3\text{O}_{12}$ phase. The ratio of the two phases is 1:1 and they possess similar lattice parameters. The hopping distances of the Na^+ ions and the size of the bottleneck for Na^+ conduction were calculated and explained the high conductivity of the sample.

1. Introduction

The search for high sodium ion conduction in ceramic materials already focused on the class of NASICON-type ionic conductors in the late 1970s [1]. Very recently, very high conductivity values were achieved with this class of ceramic materials [2,3] giving new impetus for their use as solid-state electrolytes in low-temperature sodium batteries [3,4,5]. In order to understand the high conductivity in this class of ceramic electrolyte materials, a compositional guideline for high ionic conduction was

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Keywords: neutron diffraction, NASICON, crystal structure, ionic conductivity

proposed using available literature data [6]. This revealed that high ionic conductivity can be reached when the size of the M cation in the general formula $AM_2(PO_4)$ is close or equal to the size of sixfold coordinated Zr^{4+} (0.72 Å [7]). In addition, using aliovalent substitution of P with Si ($Na_{1+x}M_2^{IV}Si_xP_{3-x}O_{12}$) and/or on the M-site ($Na_{1+x+y}M_{2-y}^{IV}M_y^{III}Si_xP_{3-x}O_{12}$) and assuring electroneutrality by changing the amount of Na per formula unit, the optimal Na concentration was found to be around 3.2-3.5 mole per formula unit.

Using this guideline, the solid solutions $Na_{3+x}Sc_2Si_xP_{3-x}O_{12}$ [8] and $Na_{3+x}Sc_xZr_{2-x}Si_2PO_{12}$ [2,9,10] were studied and maximum conductivity values were obtained for $x = 0.4$ in both series [2]. In order to understand the structure-property-chemical bonding relationships, detailed crystallographic data are needed. In [8], preliminary X-ray diffraction (XRD) data were used for the solid solution $Na_{3+x}Sc_2Si_xP_{3-x}O_{12}$ but the Si and P atoms could not be distinguished and the position and site occupancy of the very mobile Na atoms was only determined with limited accuracy.

In this work, the highly conductive $Na_{3.4}Sc_2Si_{0.4}P_{2.6}O_{12}$ was further investigated using neutron powder diffraction allowing the more accurate refinement of the Na, Si and P atoms. In addition, measurements were also carried out at 100 K to reduce the mobility of Na^+ ions in the structure for better determination of positions and site occupancy factors.

2. Experimental

$Na_{3.4}Sc_2Si_{0.4}P_{2.6}O_{12}$ was synthesized by a conventional solid-state reaction using a stoichiometric amount 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 %). The mixture was heated at 300 K h^{-1} to 1173 K for 4 h. The calcined powder was ground, then annealed at 1553 K for 20 h. The obtained powder was milled in ethanol with ZrO_2 milling balls. After drying, the material was annealed again at 1373 K to eliminate traces of water or CO_2 on the sample. The powder was stored in an argon-filled glove box until used for further processing. For sample preparation, the powder was pressed into pellets and sintered at 1553 K for 10 h.

The stoichiometry of the powder was controlled by inductively coupled plasma optical emission spectroscopy (ICP-OES). 10 mg of powder was mixed with 0.25 mg lithium borate in a platinum crucible and heated for 0.5 h at 1273 K. The liquefied material was dissolved in 30 mL HCl (5 %) and made up to 50 mL volume with distilled water. The measurement was carried out using the Thermo Scientific iCAP7600 spectrometer with optical scale and CID semiconductor detector, axial and radial reflection, and wavelengths between 166 nm and 847 nm.

Neutron diffraction data were collected at 100 K and 300 K on the time-of-flight (TOF) diffractometer POWGEN at the Spallation Neutron Source in Oak Ridge National Laboratory. One set of data was collected for each temperature in the range of TOF from 9716 μs to 140000 μs (corresponding to d -spacing between 0.3 and 6.2 $\text{\AA}$) with the centre wavelength of 1.333 $\text{\AA}$. The crystallographic data were refined using the software Jana 2006 [11]. The background was fitted by manually set points using a polynomial interpolation and the peak profiles were modelled using pseudo-Voigt functions with back-to-back exponentials. The quality of the fitting was checked with the indicators R_p (R-pattern), R_{wp} (R-weighted pattern) and GoF (goodness of fit).

After sintering at 1553 K, the density of the pellets was determined using the Archimedes method and was approximately 93 % of theoretical density. The conductivity of these pellets was measured in air as described earlier [2,8] with a multi-potentiostat VMP-300 from Bio-Logic SAS, France. Gold was used as the blocking electrodes sputtered on both sides of the pellets. The frequency range used was 1 Hz - 7 MHz at intervals of 20 points per decade with an amplitude of 50 mV.

3. Results

Le Bail profile fitting

The profile fitting was carried out using the refined unit cell parameters obtained from the XRD pattern of $\text{Na}_{3.4}\text{Sc}_2\text{Si}_{0.4}\text{P}_{2.6}\text{O}_{12}$, which showed only one rhombohedral phase with space group $R\bar{3}c$ and less than 3 % of a monoclinic phase with space group $C2/c$, a structural subgroup of the first phase [8]. However, the refinement of the profile parameters of the neutron diffraction data with space group $R\bar{3}c$ alone did not result in satisfactory residuals ($GoF/R_p/R_{wp} = 4.4/6.4/3.8$ at 100 K) and the inspection of peak profiles revealed small broadenings and shoulders. Therefore the second monoclinic phase was added. The final quality of the fitting was $GoF/R_p/R_{wp} = 2.11/3.86/1.9$ at 100 K and 1.48/2.87/1.28 at 300 K. The Le Bail fitting clearly revealed that the powder contains a mixture of monoclinic and rhombohedral phases.

Rietveld refinement

The Rietveld method was used to refine the atomic parameters and isotropic thermal parameters. The zero shift and sample displacement parameter were kept the same for both 100 K and 300 K temperatures. Using XRD, it was not possible to refine the occupancy of P and Si because of their similar atomic scattering factors. In contrast, all atoms can be readily distinguished from each other with neutron scattering because of their different nuclear scattering lengths, especially Si and P with 4.149 fm and 5.130 fm, respectively [12].

The occupational parameters of the P, Si and Na atoms were then refined step by step with respect to their thermal displacement and interatomic distances.

For both temperatures Si was found to be only present in the rhombohedral phase. The phase fractions at 300 K and 100 K are similar within the range of standard deviation – 50% rhombohedral and 50 % monoclinic. Considering the nominal composition of the powder and assuming the absence of additional phases, the P/Si ratio was constrained at 2.2/0.8 in the rhombohedral phase.

Table 1: Crystallographic and structural data of both phases in $\text{Na}_{3.4}\text{Sc}_2\text{Si}_{0.4}\text{P}_{2.6}\text{O}_{12}$ determined from neutron diffraction patterns. The values in bold numbers refer to the measurement at 100 K.

Phase	$\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$	$\text{Na}_3\text{Sc}_2\text{P}_3\text{O}_{12}$
Formula weight / $\text{g}\cdot\text{mol}^{-1}$	459.9	443.8
Crystal system	rhombohedral	monoclinic
Space group, Z	$R\bar{3}c$, 6	$C2/c$, 4
Phase fraction / wt%	52(3) / 60(3)	48(3) / 40 (3)
$a / \text{\AA}$	8.9884(6) / 8.9836(2)	15.5412(9) / 15.5489(8)
$b / \text{\AA}$		8.9783(5) / 8.9819(4)
$c / \text{\AA}$	21.992(3) / 22.2313(4)	9.0330(5) / 9.0674(3)
$\beta / ^\circ$		125.14(4) / 124.73(4)
$V / \text{\AA}^3$	1538.7(2) / 1553.8(6)	1030.7(11) / 1040.74(10)
$r_c / \text{g}\cdot\text{cm}^{-3}$	2.9779 / 2.9489	2.8600 / 2.8325
TOF range / μs	9716 - 140000	
Refinement method	full matrix least square against F^2	
Data points ; number of parameters	2861 ; 78 / 2861 ; 77	
R_p ; R_{wp} ; GOF (all data)	6.20 ; 4.07 ; 4.76 / 5.95 ; 3.71 ; 4.34	

Refinement of site occupation factors for Na sites resulted in a nearly charge-balanced formula. In the final cycle of the refinement, the total Na content was fixed to give a strictly electron-neutral formula. For both temperatures, the refinement of all positional, occupation, and thermal displacement parameters led to the following formulas: $\text{Na}_3\text{Sc}_2\text{P}_3\text{O}_{12}$ for the monoclinic phase and $\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$ for the rhombohedral phase. At 300 K, the rhombohedral phase contains 3 Wyckoff positions for Na as described by Guin et al. [8], where the Na(3) position represents a displacement of the Na(2) position. At 100 K, the sodium ions are less mobile and the Na(3) position was unoccupied. Nevertheless, the Na(2) site was refined with anisotropic displacement parameters leading to ellipsoids. Table 1 shows the refinement values for both phases at 100 K and 300 K and the refined diffraction patterns are plotted in Figure 1. Atomic parameters and equivalent displacement parameters are given in Table 2 and Table 3, respectively.

Figure 1: Rietveld refinement of TOF powder neutron diffraction patterns of $\text{Na}_{3.4}\text{Sc}_2\text{Si}_{0.4}\text{P}_{2.6}\text{O}_{12}$. Calculated data are shown as red dots, observed ones as a black line and the difference between them is plotted as a blue line at the bottom. Vertical markers below the diffraction patterns indicate the positions of the Bragg reflections of both phases: Phase #1: monoclinic, phase #2: rhombohedral.

Table 2: Positional and isotropic displacement parameters [$\text{\AA}^2$] of the rhombohedral phase in nominal $\text{Na}_{3.4}\text{Sc}_2\text{Si}_{0.4}\text{P}_{2.6}\text{O}_{12}$ (standard deviations are in brackets). The values in bold numbers refer to the measurement at 100 K.

Atom	Wyckoff position	Occupancy	x	Y	z	$U_{\text{eq}}/U_{\text{iso}}$
Rhombohedral $\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$ phase						
Sc	$12c$	1	0	0	0.1480(3)	0.0037(10)
		1	0	0	0.1482(4)	
P / Si	$18e$	0.73 / 0.27	0.294(2)	0	0.25	0.003(2)
		0.73 / 0.27	0.293(2)	0	0.25	
O1	$36f$	1	0.193(2)	-0.0185(17)	0.1921(5)	0.015(2)
		1	0.188(2)	-0.022(2)	0.1936(6)	0.029(4)
O2	$36f$	1	0.1884(14)	0.1717(14)	0.0852(5)	0.0082(17)
		1	0.1915(19)	0.1717(19)	0.0878(5)	0.017(3)
Na1	$6b$	0.80	0	0	0	
		0.70	0	0	0	
Na2	$18e$	1	0.606(4)	0	0.25	
		0.62	0.636(5)	0	0.25	0.015(8)
Na3	$36f$	0.20	0.985(12)	0.690(11)	0.943(4)	0.015(8)
<u>Anisotropic displacement parameters</u>						
Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sc	0.005(2)	0.005(2)	0.018(4)	0.0024(10)	0	0
Na1	0.010(15)	0.010(15)	0.07(5)	0.005(8)	0	0
	0.08(7)	0.08(7)	0.01(4)	0.04(3)	0	0
Na2	0.17(3)	0.05(3)	0.12(4)	0.024(13)	0.036(14)	0.07(3)

Table 3: Positional and isotropic displacement parameters [$\text{\AA}^2$] of the monoclinic phase in nominal $\text{Na}_{3.4}\text{Sc}_2\text{Si}_{0.4}\text{P}_{2.6}\text{O}_{12}$ (standard deviations are in brackets). The values in bold numbers refer to the measurement at 100 K.

Atom	Wyckoff position	Occupancy	x	Y	z	$U_{\text{eq}} / U_{\text{iso}}$
Monoclinic $\text{Na}_3\text{Sc}_2\text{P}_3\text{O}_{12}$ phase						
Sc	$8f$	1	0.3979(19)	0.252(5)	0.4438(17)	0.0093(19)
		1	0.3996(12)	0.248(3)	0.4481(16)	0.012(2)
P1	$8f$	1	0.644(5)	0.391(7)	0.733(7)	0.013(10)
		1	0.643(2)	0.395(5)	0.737(6)	0.011(7)
P2	$4e$	1	0.25	-0.046(14)	0.75	0.02(2)
		1	0.25	-0.072(8)	0.75	0.021(12)
O1	$8f$	1	0.544(4)	0.353(7)	0.603(6)	0.016(9)
		1	0.550(2)	0.328(4)	0.589(5)	0.004(5)
O2	$8f$	1	0.567(5)	0.059(7)	0.902(8)	0.020(11)
		1	0.573(3)	0.036(6)	0.944(6)	0.030(9)
O3	$8f$	1	0.674(4)	0.371(7)	0.958(6)	0.019(10)
		1	0.640(4)	0.349(9)	0.897(8)	0.047(14)
O4	$8f$	1	0.336(4)	0.428(7)	0.241(5)	0.005(8)
		1	0.344(3)	0.434(6)	0.267(6)	0.024(9)
O5	$8f$	1	0.575(4)	0.142(7)	0.234(6)	0.007(8)
		1	0.578(3)	0.144(5)	0.240(7)	0.014(7)
O6	$8f$	1	0.755(4)	0.169(7)	0.226(5)	0.012(11)
		1	0.758(3)	0.177(5)	0.225(6)	0.011(6)
Na1	$4c$	0.61	0.25	0.25	0	0.01(2)
		0.58	0.25	0.25	0	0.04(3)
Na2	$8f$	1	0.817(6)	0.441(9)	0.218(8)	0.018(17)
		0.95	0.808(5)	0.466(9)	0.205(9)	0.034(13)
Na3	$4e$	0.39	0.5	0.34(3)	0.25	0.01(2)
		0.5	0.5	0.43(3)	0.25	0.034(13)

4. Discussion

Structural relationship between the monoclinic and rhombohedral structure

The monoclinic and rhombohedral structures of the NASICON materials were analysed and compared in detail by Colin et al. [13] for pure $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$, where these structures occur after three different synthesis routes at different temperatures. The authors emphasized that synthesis conditions are critical for phase formation. The two crystal structures are closely related, and the main differences can be summarized as follows: The monoclinic structure presents (a) ordering of Na^+ ions/vacancies, (b) a slightly distorted crystal lattice, and (c) ordering of PO_4 tetrahedra (in the rhombohedral structure they show rotational disorder).

In the present case, approximately equal amounts of monoclinic and rhombohedral phases are present in the same sample. The monoclinic phase does not contain any Si, which is exclusively incorporated into the rhombohedral phase. Despite the different Si content and the different ionic radii for fourfold-coordinated Si or P (0.26 Å and 0.17 Å [7]), the molar volume of both phases is almost equal. This is in contrast to the behaviour observed by Guin et al. for the solid solution series [8], where the molar volume increases with increasing Si content. This shows that the synthesis conditions are indeed very important for the crystal structure obtained after the final heat treatment and that reproducible preparation requires very accurate adherence to the experimental conditions.

Ordering of Na ions and pathway for the Na conduction

The pathways of Na^+ ions in both the rhombohedral and monoclinic NASICON structure have already been described in the first report on NASICON material by Hong et al. [1,14]. The Na^+ ions jump from one position to the next through oxygen triangles (denoted as T1 and T2), the bottlenecks for Na^+ conduction. For good Na^+ conductivity, the following conditions need to be met: (a) the Na-Na distances should be close to 3.4 Å, which was found to be the optimum hopping distance [8] and (b) the triangle for this jump should be as large as possible.

In the rhombohedral phase, the conduction occurs from the Na(1) to the Na(2) position or its displacement, the Na(3) position, so that the sequence can be written as Na(1) - Na(2) - Na(1) and Na(1) - Na(3) - Na(1) at room temperature. One Na-polyhedra chain along which the Na^+ ions are mobile is shown in Figure 2b, where the ScO_6 octahedra and $(\text{P/Si})\text{O}_4$ tetrahedra are not shown for the sake of clarity. The hopping distances for both pathways are summarized in Table 4. No other pathway can be considered because the hopping distances are not favourable (< 3 Å or > 4 Å).

At 100 K, the Na(3) position is not populated, but the thermal parameters of the atoms on Na(2) sites indicate a slight displacement towards this position (Figure 22a), which means that at low temperature the Na^+ mobility is reduced but both structure models are in agreement. In addition, at both 100 K and 300 K, Na^+ hopping in the structure is isotropic and the Na(1) atoms are sixfold coordinated by Na(2)

atoms resulting in a three-dimensional conduction path. At 100 K, the Na(1)-Na(2) atomic distance is reduced to 3.32 Å (compared to 3.41 Å at 300 K) and the Na(2) position is fully occupied.

For the single-phase rhombohedral $\text{Na}_{3.4}\text{Sc}_2\text{Si}_{0.4}\text{P}_{2.6}\text{O}_{12}$ material [8], the first pathway Na(1)-Na(2)-Na(1) corresponds to a jump length of 3.43 Å and the second pathway Na(1)-Na(3)-Na(1) has alternate hopping distances of 2.95 Å and 3.78 Å at room temperature. These values do not represent any significant differences compared to the rhombohedral phase here in the two-phase sample (see Table 4). The T1 area for the first pathway, 5.23 Å [8], is smaller than the value of 5.30 Å in the corresponding phase of the two-phase sample.

Figure 2: Connection of Na-polyhedra chains in $\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$. (a) represents the Na(1)-Na(2)-Na(1) structure cut-out at 100 K, and (b) a model of disordered chains Na(3)/Na(2)-Na(1)-Na(2)/Na(3) at 300 K. O^{2-} ions are located at the corners of the polyhedra (red spheres). In both figures the triangle T1 is drawn with pale red colour.

Table 4: Wyckoff positions and site occupancy for the Na^+ ions in the rhombohedral $\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$ phase and interatomic distances along the pathways for Na conduction.

T	Site occupancy	Atomic distances along the pathway and T1 area	
		Na(1) – Na(2) – Na(1) / T1	Na(1) – Na(3) – Na(1) / T1
100 K	Na(1) <i>6b</i> 80 %	3.32(1) Å / 5.13 Å ²	/
	Na(2) <i>18e</i> 100 %		
300 K	Na(1) <i>6b</i> 70 %	3.41(3) Å / 5.30 Å ²	3.00(10) Å, 3.90 (7)Å / 5.30 Å ² , 5.66 Å ²
	Na(2) <i>18e</i> 62 %		
	Na(3) <i>36f</i> 20 %		

For monoclinic NASICON materials, there are three Wyckoff positions for the sodium ions. Similar to the rhombohedral structure, conduction occurs by jumping from the Na(1) to the Na(2) or Na(3) sites through oxygen triangles. The first pathway Na(1)-Na(2) is similar to the case of the rhombohedral structure and is shown in Figure 3a, the second pathway is depicted in

Figure 3, while the interatomic distances are summarized in Table 5.

For the single-phase monoclinic $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ at room temperature, the first pathway $\text{Na}(1)\text{-Na}(2)\text{-Na}(1)$ has a hopping distance of 3.48 Å [13], the second pathway $\text{Na}(1)\text{-Na}(3)\text{-Na}(1)$ corresponds to a rather long and thus unfavourable hopping distance of 4.31 Å. The area T1 for the pathway $\text{Na}(1)\text{-Na}(2)\text{-Na}(1)$, 4.98 Å² [13] is smaller than the value of 5.36 Å² of the corresponding phase in the two-phase sample (see Table 5).

Figure 3: Edge-connected chains of polyhedra around Na atoms in $\text{Na}_3\text{Sc}_2\text{P}_3\text{O}_{12}$, (a) represents the chain $\text{Na}(1)\text{-Na}(2)\text{-Na}(1)$ and (b) $\text{Na}(1)\text{-Na}(3)\text{-Na}(1)$. The occupancy of the atomic positions is given in bold and normal letters for 100 K and 300 K, respectively. O^{2-} ions are located at the corners of the polyhedra (red spheres). In both figures the triangle T1 (T1') is drawn with pale red colour.

Table 5: Wyckoff positions and site occupancy for the Na^+ ions in the monoclinic $\text{Na}_3\text{Sc}_2\text{P}_3\text{O}_{12}$ phase and interatomic distances along the pathways for Na conduction.

Atom occupancy		Atomic distances along the pathway and T1 area	
		$\text{Na}(1) - \text{Na}(2) - \text{Na}(1) / \text{T1}$	$\text{Na}(1) - \text{Na}(3) - \text{Na}(1) / \text{T1}, \text{T1}'$
100 K	Na(1) 4c 61 %		
	Na(2) 8f 100 %	3.21(8) Å / 5.02 Å²	3.21(7) Å, 3.68(9) Å / 5.02 Å², 5.55 Å²
	Na(3) 4e 39 %		
300 K	Na(1) 4c 60 %		
	Na(2) 8f 95 %	3.58(12) Å / 5.46 Å ²	2.98(7) Å, 3.81(9) Å / 5.80 Å ² , 5.02 Å ²
	Na(3) 4e 50 %		

Conductivity of $\text{Na}_{3.4}\text{Sc}_2\text{Si}_{0.4}\text{P}_{2.6}\text{O}_{12}$

The two-phase sample showed a total conductivity of $3.5 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature. This value is one order of magnitude higher than the conductivity reported for each composition of both phases. In fact, single-phase monoclinic $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ and single-phase rhombohedral $\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$ have a conductivity of $0.1\text{-}8.9 \times 10^{-5} \text{ S cm}^{-1}$ [15,16,17,18,19] and $5.6 \times 10^{-5} \text{ S cm}^{-1}$ [8] at room temperature, respectively. The wide spread of conductivity data for $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ (Figure 4) again reflects the significant influence of synthesis parameters, processing and the resulting microstructure on the materials properties. It is interesting to note that no slope changes induced by phase transitions (at about 330-370 K and 440-490 K for curves 2-6 in Figure 4) are observed when the $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ is

substituted with Si. Similarly, phase transitions can be avoided, when the Sc-content is largely replaced by Zr (see curves 7-10 in Figure 4).

Figure 4: Ionic conductivity of $\text{Na}_{3.4}\text{Sc}_2\text{Si}_{0.4}\text{P}_{2.6}\text{O}_{12}$ [8], curve (1), in comparison with measurements of $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ reported in [15] (curve 2), [16] (curve 3), [17] (curve 4), [18] (curve 5) and [19] (curve 6). The conductivity at room temperature of the sample investigated in this work is shown as an open square. Furthermore, the ionic conductivities of $\text{Na}_{3+x+y}\text{Sc}_x\text{Zr}_{2-x}\text{Si}_y\text{P}_{3-y}\text{O}_{12}$ materials are shown as grey curves: $\text{Na}_3\text{Sc}_{0.2}\text{Zr}_{1.8}\text{Si}_{1.8}\text{P}_{1.2}\text{O}_{12}$ (curve 7) [9], $\text{Na}_{2.7}\text{Sc}_{0.2}\text{Zr}_{1.8}\text{Si}_{1.5}\text{P}_{1.5}\text{O}_{12}$ (curve 8) [9], $\text{Na}_3\text{Sc}_{1.5}\text{Zr}_{0.5}\text{Si}_{0.5}\text{P}_{2.5}\text{O}_{12}$ (curve 9) [9], $\text{Na}_{3.4}\text{Sc}_{0.4}\text{Zr}_{1.6}\text{Si}_2\text{PO}_{12}$ (curve 10) [2].

The obtained high conductivity may result for both structural and microstructural reasons. From a structural point of view, the large unit cell volume and the presence of two favourable Na-Na hopping distances of the monoclinic phase compared to the pure phase may contribute to the high conductivity. In the case of the microstructure, the high density, the absence of macroscopic defects such as crack-formation [8,20] and interfaces (grain boundaries) between the monoclinic and the rhombohedral phase with smaller intergranular resistance than in single-phase samples are regarded as reasons for the high conductivity.

Lattice parameters

The composition of the mixed-phase sample can be described as follows: the sample is composed of one NASICON structure with inhomogeneous distribution of Si so that two phases can be distinguished: a rhombohedral, Si-rich phase refined as $\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$ and a monoclinic, Si-free phase refined as $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$.

$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ crystallizes in two modifications, high-temperature (rhombohedral, $R\bar{3}c$) and low-temperature (monoclinic, $B2/b, C2/c, Bb$) modifications, which are connected by the iso-translational relationship of these space groups [21]. For better comparison of all reported crystal structures of the $\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$ and $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ phases, the unit cells were transformed from

space group $R\bar{3}c$ to $C2/c$. $B2/b$ and Bb settings were changed to C centring using the software on the Bilbao Crystallographic Server [22,23,24]. All resulting lattice parameters are summarized in

Table .

Both $\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$ phases in the single and mixed-phase samples have the volume per formula unit ($V/Z = V_{\text{cell}}/4$). Slight differences in lattice parameters might be explained by the 10-20 K difference in the sintering temperatures due to the use of different furnaces. The site occupation factors (sofs) of three Na atoms in both structures are very close: $\text{sof}_{(\text{Na}1)} = 72\%$, $\text{sof}_{(\text{Na}2)} = 67\%$, $\text{sof}_{(\text{Na}3)} = 13\%$ for pure $\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$ [8] compared to occupancies 70%, 62%, and 20%, respectively, for mixed-phase $\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$ (see Table 6). Our structural results (including sofs) for $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ correspond closely to the results of Collin, refined with space group $B2/b$ [13]. The volume per formula unit of the compounds listed in Table 6 is plotted as a function of total Na amount and preparation temperature in Figure 5. There is no obvious correlation between all three parameters. However, Na-deficient (< 3 Na per formula unit) phases are only obtained at sintering temperatures below 1400 K. Since the oxidation states of Sc, P, and O are fixed, the reason for Na deficiency is unclear. Aside from artefacts from the structure refinement, protons might be present thus resulting in charge-balanced formulas.

Table 6: Lattice parameters in the equivalent monoclinic cell, number of Na atoms per formula unit, their occupancy and preparation temperature for $\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ and $\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$ in the mixed-phase sample compared to the data of various single-phase materials (at $T = 300$ K). The space group and setting used in the original literature are given in brackets.

	a / Å	b / Å	c / Å	$\beta / ^\circ$	V / Z, Å ³	Na / f. u.	T _{prep} , K	Occupancy, %			Ref.
								Na1	Na2	Na3	
$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ (C2/c)	15.549	8.982	9.064	124.73	260.0	3	1553	60	95	50	this work
$\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$ ($R\bar{3}c$)	15.566	8.987	9.046	125.00	259.0	3.8	1553	70	62	20	this work
$\text{Na}_{3.8}\text{Sc}_2\text{Si}_{0.8}\text{P}_{2.2}\text{O}_{12}$ ($R\bar{3}c$)	15.646	8.996	9.033	125.43	259.0	3.8	1623	72	67	13	[8]
$\text{Na}_{3.4}\text{Sc}_2\text{Si}_{0.4}\text{P}_{2.6}\text{O}_{12}$ ($R\bar{3}c$)	15.554	8.980	9.041	124.99	258.6	3.4	1623	70	62	14	[8]
$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ ($R\bar{3}c$)	15.462	8.927	9.168	124.21	261.6	3	1743	69	92	-	[13]
$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ (B2/b, Bb)	15.404	8.919	9.103	123.53	260.6	3	fusion	50	100	50	[13]
$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ ($R\bar{3}c$)	15.502	8.950	9.034	124.89	257.0	3	1373	73	79	-	[13]
$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ (C2/c)	15.641	8.913	9.016	124.80	258.0	2.28	1323	58	60	55	[25]
$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ ($R\bar{3}c$)	15.463	8.927	9.064	124.66	257.3	3	1573	67	99	-	[16]
$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ ($R\bar{3}c$)	15.469	8.931	9.054	124.72	257.0	2.86	1373	66	88	-	[17]
$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ (Bb)	16.100	8.928	9.109	127.15	259.3	3	1373	100	100	100	[26]
$\text{Na}_3\text{Sc}_2(\text{PO}_4)_3$ ($R\bar{3}c$)	15.709	8.936	9.024	126.01	256.2	3	1373	69	92	-	[27]
$\text{Na}_3\text{Zr}_{1.5}\text{Sc}_{0.5}(\text{Si}_{0.5}\text{P}_{0.5}\text{O}_4)_3$ (C2/c)	15.616	9.019	9.184	123.92	268.3	3	1473	69	86	73	[9]
$\text{Na}_{2.5}\text{Zr}_{1.8}\text{Sc}_{0.2}(\text{Si}_{0.43}\text{P}_{0.57}\text{O}_4)_3$ ($R\bar{3}c$)	15.560	8.983	9.219	124.23	266.3	2.5	1323	63	30	16	[10]

6. Acknowledgements

The authors gratefully acknowledge the financial support provided by JCNS to perform the neutron scattering measurements at the Spallation Neutron Source (SNS), Oak Ridge, USA. Part of this research used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by Oak Ridge National Laboratory.

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