On the dependence of ionic transport on crystal orientation in NaSICON-type solid electrolytes

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Abstract
The dependence of ionic transport on crystal orientations in NaSICON-type solid electrolytes is studied on flux-grown \( \text{M}_{3}\text{Sc}_2(\text{PO}_4)_3 \) (\( \text{M} = \text{Na}, \text{Ag} \)) single crystals with well-defined facets. Herein, we provide the first impedance spectroscopy study to characterize ion conduction along different crystallographic orientations in this important class of materials for electrochemical energy storage systems. Moreover, we used single crystal x-ray diffraction, differential scanning calorimetry, \(^{23}\text{Na}\) NMR spin-lattice relaxation measurements, and \textit{ab initio} molecular dynamics simulations to study the interplay of structure and ion transport taking place at different length scales. We conclude that the phase behavior in NaSICON-type materials is strongly linked to ion diffusion. At room temperature, ionic conductivity is slightly anisotropic along the crystallographic orientations [001] and [100]. The slightly different activation energies are related to diffusion bottlenecks solely changing along [001]. This change is caused by anisotropic thermal lattice expansion. With increasing temperature, ion transport increasingly becomes isotropic finally resulting in an order-disorder phase transition from \( \text{C}_2 / c \) to \( \text{R} - 3\text{c} \). This phase transition is associated with a clear change in activation energy solely along [001]; it can be traced back to the increasing jump distance along this crystal orientation with temperature. Astonishingly, changing the ionic charge carrier, i.e. when going from \( \text{Na}^+ \) to \( \text{Ag}^+ \), shifts the phase transition temperature by 140 K towards lower temperature. The Arrhenius behavior remains, however, similar. This finding is related to the higher mobility of \( \text{Ag}^+ \) in the NaSICON framework leading to isotropic ion diffusion at much lower temperatures. Overall, flux-grown \( \text{M}_{3}\text{Sc}_2(\text{PO}_4)_3 \) allowed us to show that ionic transport parameters and phase stability sensitively depend on crystal chemistry.

1. Introduction

Fast transport of ionic charge carriers between the electrodes of a Li-ion battery or a Na-ion battery is crucial to achieve sufficiently high energy densities and high power [1]. For this reason, liquid electrolytes are usually employed in commercial cells because of their high ionic conductivities reaching values as high as \( 10^{-2} \text{ S cm}^{-1} \) at room temperature (RT) [2]. Because of serious safety concerns, particularly for larger batteries, as well as the possibility to increase the energy density of current systems, solid-state electrolytes entered the spotlight of battery research [3, 4]. To realize such devices, solid electrolytes with high RT ionic conductivities are required that exceed values of \( 10^{-3} \text{ S cm}^{-1} \). One of the most promising solid electrolytes fulfilling this requirement are NaSICON (Na-ion Super Ionic CONductor)-type materials [5, 6].

As yet, many studies have been published on ionic transport in NaSICON-type systems [7]. It is, however, still under debate which factors are responsible for the strong variation of transport properties in polycrystalline
samples. This variation is even seen for samples that are expected to be very similar with regard to chemical composition, structure, and morphology [7,8]. The origins responsible for this variation have to be identified to precisely control the transport properties of such ceramics. Of course, only materials with reproducible properties would enable a future transfer of ionic solid conductors from lab to industrial scale applications.

Among many other factors, such as impurities, the exact defect chemistry and cracks originating from residual stresses during anisotropic thermal expansion and contraction [9,10], we suppose that anisotropic ion transport is an additional factor affecting total conductivity values. Since single crystals have, so far, rarely been synthesized, only little information is available that helps understanding the interplay of structural anisotropy and ion dynamics.

Here, we prepared single crystals of Na$_3$Sc$_2$(PO$_4$)$_3$ (NSP) with well-developed facets using flux methods; for comparison, the Ag-counterpart Ag$_3$Sc$_2$(PO$_4$)$_3$ (ASP) was prepared by a chemical exchange reaction from the NSP crystals. Taken together, these model systems enabled us to study the temperature dependence of the ion conductivity as a function of the crystal orientation. Moreover, we used single crystal x-ray diffraction (SCXRD), $^{23}$Na nuclear magnetic resonance (NMR), as well as ab initio molecular dynamics (AIMD) calculations to correlate transport properties with structural features.

2. Experimental

2.1. Preparation of Na$_3$Sc$_2$(PO$_4$)$_3$ and Ag$_3$Sc$_2$(PO$_4$)$_3$

Large single crystals were prepared by a two-step process following the protocols of [11]. First, three moles of NaPO$_4$ and one mole of Sc$_2$O$_3$ were mixed and then pre-heated at a temperature of 673 K. In a second step, the finely ground and pelletized precursor was heated to 1573 K for 30 h to obtain phase pure NSP in the form of a polycrystalline sample. We used x-ray powder diffraction to prove the purity of this sample. In the actual experiment to grow single crystals, one mole of NSP is mixed with six moles of Na$_4$P$_2$O$_7$ as the high temperature flux. Afterwards, the mixture was put into a platinum crucible, covered with a lid, heated to 1573 K at a rate of 100 K h$^{-1}$ and then held at this temperature for 50 h to allow the melt to homogenize. Following this, the sample was slowly cooled down to 1573 K (3 K h$^{-1}$). Finally, it was cooled down to RT (723 K h$^{-1}$, furnace cooled). Ag$_3$Sc$_2$(PO$_4$)$_3$ were obtained via ion-exchange using the Na$_3$Sc$_2$(PO$_4$)$_3$ crystals. For this purpose, 250 mg of Na$_3$Sc$_2$(PO$_4$)$_3$ were immersed in 500 ml of an aqueous AgNO$_3$ solution under constant stirring. We observed that, for powder samples, exchange of Na$^+$ by Ag$^+$ turned out to be rather fast if we use a 1 M AgNO$_3$ solution for the leaching process. The process was finished after 30 min. To guarantee, however, full ion exchange, for the larger single crystals we increased the leaching time to 6 h, as mentioned above.

2.2. Single crystal x-ray diffraction

SCXRD data were collected on a Bruker SMART APEX charge-coupled device (CCD) diffractometer. The crystals were selected on the basis of their optical properties such as sharp extinctions, regular shape and homogeneity in colour. They were glued on top of a glass capillary (0.1 mm in diameter). Intensity data were collected with graphite-monochromatized Mo K$_\alpha$ x-ray radiation (50 kV, 30 mA). The crystal-to-detector distance was 40 mm and the detector was positioned at $28^\circ$ 2$\Theta$ using an $\omega$-scan mode strategy at four different $\phi$ positions ($0^\circ$, $90^\circ$, $180^\circ$ and $270^\circ$). Six-hundred and sixty-six frames with $\Delta \omega = 0.3^\circ$ were acquired for each run. Three-dimensional data were integrated and corrected for Lorentz-, polarization and background effects using the APEX3 software [12]. Structure solution using direct methods and subsequent weighted full-matrix least-squares refinements on $F^2$ were carried out with SHELX-2012 as implemented in the program suite WinGX 2014.1 [13,14]. Details on data collection and results of structure refinements are given in the supplement tables S1 to S3 which are available online at stacks.iop.org/JENERGY/2/035003/mmedia and the full set of data is available via the CIFs in the supplementary material.

2.3. Scanning electron microscopy

ASP single crystals were examined by Zeiss Ultra Plus Field—Emission Scanning Electron Microscope. Identification of elements on the cross section of ASP single crystals were analyzed by an Oxford Instrument (X-MAX 50 mm$^2$ SDD Energy Dispersive x-ray (EDX) spectrometry) coupled to the FE-SEM. Mapping analyses were performed at 10 kV with a working distance of 9 mm. EDX spectral integration time for point analysis was chosen as 30 s and the elemental mappings were carried out using a total integration time of 30 min per image.

2.4. Differential scanning calorimetry

The heat capacity $C_p$ of the samples (38 mg) was measured using power compensated differential scanning calorimetry (DSC, Diamond DSC Perkin Elmer). We covered a temperature range of 2 K to 573 K. DSC measurements were performed under a flow of Ar gas in step scanning mode applying a heating rate of
10 K min⁻¹ with the calorimeter block kept at 253 K using a PerkinElmer Intracooler. Each measurement consisted of a blank run with empty calorimeter chambers, a calibration, and a sample run, where the samples were placed into the sample chamber of the calorimeter. For calculating the heat capacity, the net heat flow data were finally divided by the heating rate and the mass of the sample. Each sample run was corrected against a calibration run using a synthetic single crystal of corundum (31.764 mg), whose heat capacities were taken from the National Bureau of Standards Certificate. The accuracy of the DSC heat capacity data was determined to be better than 0.6%. Low temperature caloric measurements were carried out using a Quantum Design Physical Property Measurement System (PPMS) equipped with a relaxation calorimeter option.

2.5. NMR spectra and NMR spin-lattice relaxation

²³Na NMR measurements were performed under static, i.e. non-rotating, conditions. We used a Bruker Avance III spectrometer that was connected to a shimmed cryo-magnet with a nominal magnetic field $B_0$ of 7 T. This magnetic field strength corresponds to a ²³Na Larmor frequency of $\frac{\omega_0}{2\pi} = 79$ MHz. The single crystals were fire-sealed under vacuum in a quartz glass ampule to permanently protect them from moisture and air; they were placed directly inside the NMR probe (Bruker). We measured spin-lattice relaxation rates and line shapes over a temperature ranging from 233 K to 473 K.

While NMR line shapes were recorded with so-called single pulse experiments (64 scans), the saturation-recovery pulse sequence with quadrature detection was employed to record variable-temperature diffusion-induced ²³Na NMR magnetization transients. We used a comb of ten closely spaced $\pi/2$ radio frequency pulses to destroy any longitudinal magnetization. Its recovery, which is above 233 K solely induced by diffusive hopping processes of the ²³Na quadrupole nuclei, was detected after variable waiting times $t_d$ with a $\pi/2$ reading pulse. We parameterized the resulting magnetization transients with exponential functions to extract the rate $R_1$.

At a power level of 200 W the $\pi/2$ pulse length ranged from 3.4 to 4.3 μs, depending on temperature $T$. Temperatures inside the sample chamber were monitored with a Eurotherm controller and adjusted with a stream of freshly evaporated dry nitrogen that passes a heater beneath the sample chamber. Simulations of the 1D ²³Na NMR spectra (²³Na is a quadrupole nucleus with a spin–quantum number of 3/2), obtained by Fourier transformation of the free induction decays, were carried out with WSOLIDS1 software [15].

2.6. Impedance spectroscopy

Impedance spectroscopy measurements were carried out to investigate long-range ionic transport. Ag-epoxy and Na metal were used as electrode materials to ensure contact between the stainless steel cylinders and the single crystals. The latter were placed in a ceramic sample holder. Data were recorded with a Novocontrol Concept 80 broadband spectrometer that is connected to a Quatro cryo system for temperature regulation. It is equipped with a ZGS active sample cell (Novocontrol). Complex impedances (at a voltage amplitude of 100 mV) were measured at frequencies ranging from 10 MHz to 10 mHz and in a temperature from 183 K to 373 K.

2.7. Density functional theory calculations

First-principles calculations were performed using density functional theory (DFT) as implemented in the plane-wave-basis-set Vienna ab initio simulation package (VASP) [16]. Both the ionic diffusivity and conductivity in the predicted materials were calculated using AIMD in VASP. The simulations were performed on the canonical ensemble with a time step of 2 fs, and the temperature was initialized at 100 K and elevated to appropriate temperatures (600 K, 720 K, 900 K, 1200 K and 1500 K) with simulations of about 100 ps for statistical analysis. The experimental unit-cell (SG C2/c) of NSP was used for simulation; this cell consists of six formula units. A $\gamma$-point-only sampling of $k$-space and a 400 eV plane-wave energy cutoff was used for the simulations. Na-ion diffusivities were calculated from atomic trajectories through the Einstein relation. The activation energy and its extrapolation to diffusivity at RT were obtained assuming Arrhenius behavior. Details of the simulation process can be found elsewhere [17].

3. Results and discussion

3.1. Preparation of the single crystals

The NSP single crystals were successfully synthesized by the flux method, see figure 1(A) which shows a large amount of irregular shaped transparent crystals. We handpicked single crystals with well-defined facets using a tip under an optical microscope. Special care was taken to select sufficiently large single crystals (>200 μm) with regular shapes and a large $c/a$ ratio. The latter is necessary to carry out impedance measurements on differently oriented crystals (see figure 1(B)).

As mentioned above, the ASP single crystals were prepared by chemical-exchange. EDS mapping on the cross section of a crushed single crystal confirmed the complete exchange of the ions, see figure 1(C)–(F).
The NSP single crystals investigated show a single phase transition at approximately 423 K. It shows the group-subgroup relations for the symmetry reduction down to SG $C_{c2} \rightarrow C_{c2} \rightarrow C_{2}$. At 289 K this latter polymorph converts into the $\gamma$-form (R−3c). See below for details on the phase analysis. The pathway of symmetry reduction for NSP and ASP single crystals recorded from 2 K to 300 K is highlighted in the Bäringhaus diagram of SG $C_{c2}$. (A) Crystal structure of Na3Sc2PO4·F, respectively. (B) Na-ion connectivity within the NASICON structure formed by the Na-ions. Area highlighted in red indicates the non-equivalent Na-position in the $C_{c2}$-sub-lattice. (C) Selected hand-picked Na3Sc2PO4·F single crystals with well-defined facets and large c/a ratios. (C) Scanning electron microscopy (SEM) images of a crushed Na3Sc2PO4·F single crystals after the chemical exchange of Na⁺ by Ag⁺. The chunk of the single crystal highlighted in the dashed box and magnified in (D) was used for elemental mapping. The corresponding element maps are shown in (E). Quantitative chemical analysis before and after chemical exchange are shown in (F).

3.2. Phase behavior as studied by DSC

The NSP single crystals investigated show a single phase transition at approximately 423 K (see figure 2(A)). Although the peak is broad and not very pronounced, it is unmistakable an endothermic one that can be assigned to the $\beta$-$\gamma$-phase transition. The corresponding space groups of the two modifications are $C2/c$ ($C2/c-\beta$) and $R-3c$ ($R-C2/c-\gamma$). In agreement with previous reports, ASP single crystals undergo several phase transitions, see figures 2(B) and (C) [18]. Analogous to NSP, but shifted in temperature, the first phase transition is found at approximately 180 K. It corresponds to a transition from the smaller monoclinic $\alpha$-phase with $C2/c$ ($C2/c-\alpha$) to the larger monoclinic $\beta$-phase $C2/c-\beta$. At 289 K this latter polymorph converts into the $\gamma$-form (R−3c) [19]. See below for details on the phase analysis. The pathway of symmetry reduction for NSP and ASP single crystals is highlighted in the Bäringhaus diagram of SG $R-3c$ in figure 2(D).

It shows the group-subgroup relations for the symmetry reduction down to SG $C_{c2}$ of parent SG $R-3c$ as based on the routine SUBGROUPGRAPH [20]. SG $C_{c2}$ was chosen as a probable low temperature modification of NSP, see the suggestion in [11]. It can be seen that SG $C2/c$ is a natural sub-group of SG $R-3c$. SG $C2/c$ can transform either to another $C2/c$ structure, to primitive cells or directly to $Gc$. Additionally, the symmetry reduction can proceed via SGs with trigonal symmetries. As it will be shown below, this is, however, neither true for NSP nor for ASP.
3.3. Structural details as studied by SCXRD

In earlier studies, several structural models were used to refine the super-structure reflections of the structure of NSP at RT. Neither the hexagonal unit cell \(a = b = 17.8925(16)\,\text{Å}, c = 22.2806(19)\,\text{Å},\) nor the monoclinic one (named as \(M_1\), \(a = 15.4754(3)\,\text{Å}, b = 8.9350(2)\,\text{Å}, c = 9.0350(2)\,\text{Å}, \beta = 124.815(2)^\circ\), SG \(C2/c\), which has often been proposed in literature for the structure at RT, allowed us to fully index all Bragg reflections \([7, 11]\). Full indexing is, however, possible using a tri-twinned monoclinic super cell \((M_2)\) with \(a = 15.4762(3)\,\text{Å}, b = 8.9351(2)\,\text{Å}, c = 22.2549(5)\,\text{Å}, \beta = 90.0106(5)^\circ\). While the \(a\) and \(b\) dimensions are similar in \(M_1\) and \(M_2\), the unit cell parameters \(c\) and the monoclinic angle are related to each other via

\[c_{M_2} = 3c_{M_1}\sin\beta_{M_1}.\]

We assign the larger \(M_2\) cell to the \(C2/c\)-\(\beta\) phase of the NaSICON-type structures (see figure 2(E)), while the \(M_1\) cell, as it will be shown later for \(\text{Ag}_3\text{Sc}_2(\text{PO}_4)_3\), corresponds to the low temperature \(C2/c\)-\(\alpha\) phase.

Na-Na distances, ranging from 3.38(2) to 3.44(2) Å, are given in table 1.

In terms of short contacts between neighboring Na\(^+\) ions, the most favorable paths would run via \(\text{M1A-M2C-M1B-M2D-M1B-M2C}\) (inner-chain pathway), and \(\text{M1A-M2A-M1B-M2E-M1B}\) (inter-chain pathway) (see figure 2(F)). The inter-chain pathway exhibits slightly larger distances between neighboring Na positions and, thus, may be somewhat less favored for Na-ion hopping from an energetic point of view. Indeed, the highly

| SG | \(C2/c\) | \(R-3c\) |
|----|--------|--------|
| \(T/\text{°C}\) | 20(2) | 230(2) |
| \(a/\text{Å}\) | 15.4762(3) | 8.9350(2) |
| \(b/\text{Å}\) | 8.9350(2) | 8.9350(2) |
| \(c/\text{Å}\) | 22.2549(5) | 22.5233(12) |
| \(β/°\) | 90.0106(5) | — |

| bond distances | SG | Atom 1 | Atom 2 | Distance/Å |
|----------------|----|--------|--------|-----------|
| \(C2/c\) | Na1A | Na2A | 3.416(18) |
| | Na2B | 3.416(21) |
| | Na2C | 3.392(17) |
| | Na1B | Na2A | 3.395(23) |
| | Na2B | 3.436(21) |
| | Na2C | 3.391(22) |
| | Na2D | 3.381(24) |
| | Na2E | 3.407(23) |
| | Na1 | Na2 | 3.409(1) |
| | Na11 | 1.34(1) |
| | Na22 | 1.10(6) |
| | Na2 | 1.16(4) |

| occupation and equivalent isotropic displacement parameter | \(\text{Na}_3\text{Sc}_2(\text{PO}_4)_3\) |
|----------------------------------------------------------|-----------------|
| SG | Atom | Occ/pfu | \(U_{eq}^{1/2}\) Å² |
| \(C2/c\) | Na1A | 0.24(1) | 0.115(3) |
| | Na1B | 0.48(1) | 0.108(2) |
| | Na2A | 0.47(1) | 0.0418(9) |
| | Na2B | 0.48(1) | 0.0427(9) |
| | Na2D | 0.47(1) | 0.0427(9) |
| | Na2E | 0.22(1) | 0.0460(15) |
| \(R-3c\) | Na1 | 0.66(2) | 0.177(3) |
| | Na11 | 0.31(2) | 0.065(11) |
| | Na22 | 0.23(2) | 0.065(11) |
| | Na2 | 2.19(2) | 0.0816(19) |
| \(\text{Ag}_3\text{Sc}_2(\text{PO}_4)_3\) | Ag11 | 1.01(1) | 0.0775(17) |
| | Ag21 | 0.52(6) | 0.039(8) |
| | Ag22 | 0.84(1) | 0.0418(17) |
| | Ag2 | 1.14(1) | 0.056(3) |

\(^1U_{eq}\) is defined as one-third of the trace of the orthogonalized \(U_{ij}\) tensor.
anisotropic atomic displacement parameters of Na1A and Na1B support this view. The planar-like shapes along [100] of the vibration ellipsoids indicate a preferred Na-ion transport along the inner-chain pathway (see figures 2(G) and S1). Details on data collection, fractional atomic coordinates and selected bond lengths can be found in tables S1–S3.

Towards higher temperatures, NSP transforms to the NaSICON-structure with SG $R – 3c (R – 3c – γ)$, $a = b = 8.898(3)$ and $c = 22.607(8)$ Å ($600$ K). Na"$^+$" partially occupies the typical M1 (6b) sites at (0 0 0) and the M2 (36f) sites at $(x^1/3, x^1/3, x^1/3)$, with 0.52 per formula unit (pfu) and 2.13 pfu, respectively, whereby a distinct residual electron density can be found in between these two positions. To account for this residual electron density two intermediate positions M11 and M22 where introduced in the refinement (see table S1 and figure S2). These evidently mark the diffusion path along M1-M11-M22-M2-M22 directly form the SCXRD data. The isotropic atomic displacement parameters of Na1 and the cigar-like shaped vibration ellipsoids of Na2 indicate an isotropic Na-ion transport along all crystallographic orientations (see figures 2(H) and S1).

The evolution of the lattice parameters, as based on the average SG $C2/c-β$ structures refined from SCXRD data, is highly anisotropic with a large thermal expansion along [001]. This observation is in agreement with previous studies [21].

In contrast to NSP, the crystal structure of the Ag-compound ASP shows $R – 3c – γ$ symmetry already at RT, i.e., ion exchange stabilizes the highly conducting $γ$-phase at lower temperature $T$ and distinctly widens the unit cell parameters (see table 1). The size and the distortion of the polyhedra in the NaSICON framework remains rather unchanged; individual and average P-O interatomic distances are very similar in both compounds while the Sc polyhedra appear to be the slightly larger and less distorted in Ag$_3$Sc$_2$(PO$_4$)$_3$. In agreement with the investigation of Atovmyan and Tjachev, and in line with the observed $R – 3c – γ$ structure of NSP, more than two possible Ag positions were identified [22]. Interestingly, the M1 position at 6b (0, 0, 0) is not occupied anymore and the Ag$^{+}$ are shifted to a general position 36f located at 0.017(2), 0.0807(6), 0.0019(2) which we name M11. This site is close to the original M1 position of the NaSICON framework and has to be characterized by an occupancy factor of 1.012(7) pfu. The regular M2 position at 18c also shows a high occupancy of 1.14(1) pfu; significant residual electron density nearby indicated, however, the presence of an additional position M22 for Ag; this position is 0.55 Å away from M2, with an occupancy of 0.84(1) pfu. To achieve good modelling results considering the observed electron density of Ag$^{+}$, in between M22 and M11 a further position for Ag$^{+}$, which is named M21, was necessary to include. Due to the low occupancy of 0.052(6) pfu only isotropic displacement parameters could be refined for this position. For all other Ag$^{+}$ sites, full anisotropic refinement of the atomic displacement parameters could be achieved and yield highly anisotropic, cigar-like shaped vibration ellipsoids being oriented along the most probable ion-diffusion path. Bypassing both regularly occupied positions M1 and M2 allows very short jump distances for Ag$^{+}$ to migrate along the pathway M11-M11-M21-M22-M22-M21, with distances of 0.668(3) Å, 1.352(2) Å, 1.188(2) Å, 0.501(2) Å, 0.501(2) Å, and 1.188(2) Å, respectively.

3.4. Impedance measurements

Impedance spectroscopy was used to measure ion transport properties of the single crystals along the directions [001] and [100]. The setup of our measurements is illustrated in figure 3(A) and (B).

Exemplarily, Nyquist plots of impedance data, that is, the imaginary part, $Z_{im}$ of the complex impedance is shown as a function of its real part, $Z_{re}$ in figures 3(C) and (D). The complex plane plots refer to 180 K and 373 K, respectively. Coming from high frequencies, the Nyquist plot recorded at 180 K is composed of a single semicircle directly followed by a sharp electrode spike that appears in the low frequency regime. The latter is typically seen for fast ion conductors whose complex impedance values are recorded with the help of ion blocking electrodes. The electrode response can be described with a resistor (R) connected in parallel to a constant phase element (CPE). The semicircle seen at high frequencies can be parametrized with the same R-CPE unit. The capacitance of this unit is given by $C = (R^{-1} \times n \times \text{CPE})^{1/n}$, whereby $n$ accounts for the non-ideal behavior of the capacitance.

Here, we obtain $C = 0.1$ pF. In general, values in the order of some pF are typically assigned to electrical processes taking place in the interior of the grains.

As the characteristic electrical frequency ($\omega_c = 1/RC$) shifts towards higher frequencies with increasing temperature $T$ the bulk semicircle fully disappears in the complex plane plots recorded at elevated $T$ (see figure 3(D)). Hence, the impedance spectrum of NSP measured at 373 K is dominated by the electrical response of the ion-blocking electrodes. At this temperature, the bulk response would be fully visible only at frequencies reaching the GHz regime. The electrode response can be described with a R-CPE unit, which is needed to estimate the bulk resistance. The latter is simply approximated with a single resistor connected in series to the R-CPE unit. The bulk ion conductivities $\sigma_{\text{bulk}}$ are given by $\sigma_{\text{bulk}} = d/(R_{\text{bulk}}A)$ with $A$ being the area of the electrode and $d$ denoting the thickness of the sample. Here, $\sigma_{\text{bulk}}$ along [001] turned out to be $8.0 \times 10^{-4}$ S cm$^{-1}$. For $\sigma_{\text{bulk}}$ along
we obtained 5.4 × 10^{-4} \text{ S cm}^{-1}. These values are in good agreement with values reported for polycrystalline NSP (see, for example, [11, 23, 24]) corresponding to a slight anisotropy given by \( \sigma_{\text{bulk},[001]} / \sigma_{\text{bulk},[100]} \approx 1.48. \)

Nyquist plots for ASP recorded at \( T < 283 \text{ K} \) and \( T \geq 283 \text{ K} \) are shown in figures 3(H) and (I), respectively. The complex plane plot referring to Ag_3Sc_2(PO_4)_3, which was recorded at 183 K, is again composed of a semicircle appearing at high frequencies and a sharp electrode spike at lower values of \( \omega \), see figure 3(H). As for the NSP single crystals, the location curve can be fitted using two R-CPE units connected in series. At 313 K we used a resistor and an R-CPE unit to parameterize our data, see figure 3(I). At RT we obtained the following values for \( \sigma_{\text{bulk}} \): 4.8 × 10^{-3} \text{ S cm}^{-1} \) along [001] and 2.6 × 10^{-3} \text{ S cm}^{-1} \) along the [100] direction yielding

Figure 3. (A,B) Experimental setup used to carry out impedance measurements depending on crystal orientation. Two stainless steel cylinders (1 mm in diameter each) are placed in a ceramic sample holder with drilled holes (A). The single crystals of Na_3Sc_2(PO_4)_3 and Ag_3Sc_2(PO_4)_3 were placed between the cylinders and contacted either with a thin layer of Ag-Epoxy or Na metal (B). Complex plane plots of impedance data of Na_3Sc_2(PO_4)_3 single crystals recorded along the [001] direction at \( T = 183 \text{ K} \) (C) and \( T = 373 \text{ K} \) (D). Solid lines represent fits with the equivalent circuits indicated. Dashed lines reveal the contributions of the individual components of the circuits. (E) Arrhenius plot showing the temperature behavior of the Na-ion conductivities measured at temperatures ranging from 230 K to 473 K. Whereas filled symbols refer to Na-ion transport along [100], open circles represent ionic conductivities along the [001] direction. Ionic conductivities measured with Na metal electrodes are represented by squares (C). (F) Complex plane plot of the electrical impedance of Na_3Sc_2(PO_4)_3 single crystals recorded along the [001] direction at a temperature of 296 K. Data were acquired with the help of ohmic Na electrodes. (G) Magnification of the semicircle seen in the high frequencies range (F). Nyquist plots of the Ag_3Sc_2(PO_4)_3 single crystals recorded along [001] at 183 K (H) and at 313 K (I). Solid lines show fits with the equivalent circuits indicated. Again, dashed lines reveal the individual contributions of the two components. (J) Arrhenius plot of the temperature dependence of the Ag-ion conductivity of single crystalline Ag_3Sc_2(PO_4)_3 (183 K to 313 K). Whereas filled symbols refer to Ag-ion transport along [100], open circles represent ionic conductivities along the [001] direction. Ionic conductivities measured with Na metal electrodes are represented by squares (C).
In order to validate the accuracy of the fitting procedure used above for ion-blocking electrodes further impedance measurements were carried out at 296 K using a non-blocking Na metal ohmic electrode. If non-blocking metal electrodes are used, the corresponding Nyquist plot is also composed of two semicircles, the semicircle at high frequencies characterizes again ion transport in the bulk regions, the other one represents the interface capacitance.

The use of non-blocking electrodes helps separating the bulk process from the total response as strong polarization effects are absent in cases. The whole electrical response can be well described with two R-CPE units connected in series. Based on the capacitance of approximately $C_{\text{bulk}} = 2 \, \text{pF}$, we assign the high frequency semicircle to an inner grain relaxation process. The corresponding values $\sigma_{\text{bulk}}$ along the directions $[001]$ and $[100]$ are $8.0 \times 10^{-4} \, \text{S cm}^{-1}$ and $5.4 \times 10^{-4} \, \text{S cm}^{-1}$, respectively. These values agree with those obtained using ion-blocking electrodes, vide supra. The low frequency relaxation process has to be characterized by a capacitance of approximately $C_{\text{int}} = 10 \, \text{nF}$. We assume that the underlying electrical relaxation process corresponds to a charge transfer process that is characterized by the resistance $R_{\text{t}}$. The corresponding area specific resistance (ASR), along $[001]$ and $[100]$, is given by $\text{ASR} = R_{\text{t}} A / 2$ and turned out to be $122 \, \Omega \, \text{cm}^2$ and $55 \, \Omega \, \text{cm}^2$, respectively.

For the ASP single crystals, we also used Na as a quasi ohmic electrode to validate the results obtained with ion-blocking electrodes. Although the interface resistance is relatively large for ASP, the Nyquist plots reveal a similar impedance behavior as seen for NSP. Thus, we were able to accurately determine the corresponding bulk Ag-ion conductivities along the two directions of interest, viz. along $[001]$ and $[100]$. They take the following values $\sigma_{\text{bulk},[001]} = 0.40 \times 10^{-3} \, \text{S cm}^{-1}$ and $\sigma_{\text{bulk},[100]} = 2.4 \times 10^{-3} \, \text{S cm}^{-1}$, respectively. Again, these values are in excellent agreement with the values obtained using ion-blocking electrodes.

For the ASR, Table 2 summarizes the results from our impedance measurements.

Finally, we used the bulk Na-ion conductivities to estimate solid-state diffusion coefficients $D$ according to the Nernst- Einstein equation

$$ D = \sigma_{\text{bulk}} k_B T \left( N q^2 \right)^{-1} \quad \text{where } k_B \text{ denotes Boltzmann’s constant, and } q \text{ the elementary charge of the mobile ions.}$$

$N$ refers to the number density of charge carriers, which we calculated from our SCXRD data. We obtained the following values: $D_{[001]} = 0.98 \times 10^{-12} \, \text{m}^2 \, \text{s}^{-1}$ and $D_{[100]} = 0.66 \times 10^{-12} \, \text{m}^2 \, \text{s}^{-1}$ for NSP; $D_{[001]} = 6.7 \times 10^{-12} \, \text{m}^2 \, \text{s}^{-1}$ and $D_{[100]} = 3.6 \times 10^{-12} \, \text{m}^2 \, \text{s}^{-1}$ for ASP.

In figure 3(I) the temperature dependence of $\sigma_{\text{bulk}}$ of NSP, obtained from measurements with ion-blocking electrodes, along the directions $[100]$ and $[001]$ is shown. It follows Arrhenius behavior according to $\sigma_{\text{bulk}} T = \sigma_0 \exp \left(-E_{\text{ab}}/(k_B T)\right)$, where $\sigma_0$ represents the pre-exponential factor. Interestingly, a knee at ca. 423 K is observed for $\sigma_{\text{bulk}}$ characterizing ion transport along $[001]$. We assign this change in temperature behavior to the phase transition observed by DSC. The activation energies $E_{\text{ab}}$ along $[001]$ and $[100]$ for $T < 423 \, \text{K}$ are 0.40 eV and 0.43 eV, respectively. These values are in good agreement with results from DFT calculations on NaSICON-type
Na$_3$Zr$_2$(SiO$_4$)$_3$(PO$_4$)$_2$ revealing a similar trend [26]. Importantly, ionic transport for $T \geq 423$ K along [001] has to be characterized by a significantly reduced activation energy of only 0.25 eV.

As mentioned above, the NaSICON-type framework consist of two possible diffusion pathways for the ions: an inter-chain pathway along [001] and an inner-chain pathway along [100] = [010], see also [26]. Since Na-ion diffusion strongly depends on the bottleneck size, jump distance, as well as on the Na-ion distribution, a strong temperature dependency of the ion conductivity is expected [7, 27, 28]. The bottleneck size and its shape along the different pathways is related to the lattice parameter, which changes along [001]. In contrast, it remains almost constant for [100]. Therefore, the increase in bottleneck size in the [001] direction, which is not observed for [100], may lead to a steeper increase in Na-ion conduction and could explain the slightly higher activation energy observed. At ca. 340 K Na-ion transport becomes almost isotropic (see figure 4) due to the increasing delocalization of the Na$^+$ in the NaSICON framework with increasing temperature.

This behavior is responsible for a continuous decrease of the superlattice reflections, which completely vanish at even higher temperatures; finally, at 423 K the phase transition from C2/c/β to R–3c–γ is initiated.

Within the R–3c–γ phase regime ($\geq 423$ K), the conductivity along [001] is considerably less thermally activated compared to Na-ion transport along [100]. This finding can be traced back to the anisotropic thermal lattice expansion. The most significant structural changes are found in the Na-O distances and the thermal expansion parameters of Na and O [21]. Interestingly, the root mean square displacement, $d_{\text{rms}}$, as a function of temperature of all elements has been shown to follow linear behavior, except for Na2. This feature suggests, at least for high temperatures, an increasingly hindered thermal motion of Na$^+$ through the M1–M2 bottleneck along [001]. Hence, the lower activation energy seen for Na-ion conduction along [001] is presumably caused by an opposed process, which effectively slows down the temperature dependency of $d_{\text{rms}}$ of Na2 at high temperatures [21]. Moreover, this process might lower the attempt frequency of successful Na2 jumps along [001], which results in a decreased pre-exponential factor of the underlying Arrhenius relation. Indeed, we found that the pre-factor along [001] decreases from 6.1 to 4.4 after the phase transition.

The Arrhenius plots of the conductivity behavior of the Ag$_3$Sc$_2$(PO$_4$)$_3$ single crystals are presented in figure 3(j). Similar to NSP, the lower activation energy for ionic transport along [001] is related to both an increasingly hindered ion transport through the M1–M2 bottleneck and an increasing jump distance caused by anisotropic lattice expansion. At lower temperatures an order–disorder transition from R–3c–γ $\rightarrow$ C2/c/β is observed. This transition is connected to a decreasing bottleneck size along the [100] direction. It is associated with an increasing residence time of Ag$^+$ located at the M2/M22 positions. At approximately 283 K the mean Ag$^+$ residence time at the M2/M22 position is long enough to lead to an order–disorder transition.

We expect a second change in the activation energy because of the C2/c/β $\rightarrow$ C2/c/α phase transition occurring at ca. 173 K (see above). Unfortunately, we were, so far, not able to record conductivity values in this low temperature range. Hence, further studies are needed to understand the interrelation of ionic transport and phase behavior in the low temperature region of Ag$_3$Sc$_2$(PO$_4$)$_3$. 

![Figure 4. Illustration how possible ion diffusion pathways energetically change in NaSICON-type structures with increasing temperature. The anisotropic lattice expansion varies bottleneck sizes and jump distances along the different crystallographic directions.](image-url)
3.5. Ion self-diffusion as seen by 23Na NMR

To further evaluate the Na\(^+\) hopping processes in NaSICON-type materials we used 23Na NMR to shed light on the elementary jump processes to which line-shape measurements and spin-lattice relaxation rates are sensitive \([29, 30]\). Short radio frequency pulses were used to ensure non-selective excitation of the central transition of the 23Na nucleus. The corresponding spectra are shown in Figure 5(A).

The large quadrupole moment of 23Na (spin-quantum number \(I = \frac{3}{2}\)) causes the central line to be affected by second-order quadrupolar interactions. Although rapid ion hopping processes are present in Na3Sc2(PO4)3, at temperatures below 253 K the line becomes dipolarly broadened because Na\(^+\) hopping is no longer able to average homonuclear dipole-dipole couplings. At 273 K the shape of the line sharpens because of motional averaging. In this temperature range (regime I, see figure 5(B)), simulations of the lines reveal that the isotropic shift \(\Delta \delta_{iso}\) of the central line is approximately 10 ppm. The corresponding quadrupole coupling constant turned out to be in the order of \(C_Q = 1.60 \text{ MHz}\). Below RT the electric field gradient (EFG) sensed by the 23Na nuclei seems to be best described by an asymmetry parameter of \(\eta \approx 0.5\). We clearly see that at above 310 K the shape of the central line changes; the simulations tell us that the chemical shift anisotropy \(\Delta \sigma\) reduces from \(-40\) ppm to \(-5\) ppm. In addition, in this temperature range (regime II) the ions sense an axially symmetric EFG (\(\eta \approx 0\)). This change might be related to a change in the local environment of the Na-ions in the NaSICON-type structure.

![Figure 5](image_url)

Figure 5. (A) Variable-temperature 23Na NMR spectra (central line, 79 MHz) of single crystalline Na3Sc2(PO4)3 recorded at 79 MHz at the temperatures indicated. Second-order quadrupolar interactions causes the central line to adopt the shape of a split line. Simulations of two spectra recorded at low temperatures are shown in (B). Only at sufficiently high temperatures dipole-dipole interactions (\(>253\) K) and electric quadrupolar interactions (\(>313\) K) become averaged due to Na-ion dynamics. At 393 K, where the electric quadrupole interactions dominate the spectra at low \(T\) are clearly averaged, the rate \(R_1\) passes through a diffusion-induced rate peak. (C) Arrhenius plot of the 23Na spin-lattice rates \(R_1\) of single crystalline NSP recorded in the laboratory frame of reference at 79 MHz. The dashed line shows a BPP-type fit to determine the activation energies of both the low- \(T\) and high- \(T\) flank of the peak. In the high- \(T\) limit the flank corresponds to 0.36 eV. The asymmetry of the peak is a typical feature for 3D correlated ion dynamics. The asymmetry parameter turned out to take a value of \(\beta = 1.55\). (D) \(R_1\) magnetization transients from which the 23Na NMR spin-lattice relaxation rates \(R_1\) = 1/\(T_1\) were extracted by parametrizing the curves with stretched exponentials according to \(M(t) = M_0 \exp \left( -t / T_1 \gamma \right) \).

The lower graph shows that the exponent \(\gamma\) ranges from 0.7 to 1.0. (E) Na- ion probability densities in Na3Sc2(PO4)3. The probability densities are obtained from the trajectories in the AIMD simulations at 900 K with 100 ps; the isosurfaces are plotted at isovales of the mean value of the density. (F) Temperature behavior of the calculated diffusion coefficients through AIMD simulations. The solid line shows the extrapolation towards lower temperatures (393 K).

3.5. Ion self-diffusion as seen by 23Na NMR

To further evaluate the Na\(^+\) hopping processes in NaSICON-type materials we used 23Na NMR to shed light on the elementary jump processes to which line-shape measurements and spin-lattice relaxation rates are sensitive \([29, 30]\). Short radio frequency pulses were used to ensure non-selective excitation of the central transition of the 23Na nucleus. The corresponding spectra are shown in figure 5(A).

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which agrees with the increasing isotropic conduction behavior as observed by impedance spectroscopy (see above). If the anisotropy would be more dominant, e.g., because of changes in stoichiometry [31], this slight change seen in NMR spectroscopy might be related to an order-disorder transition as reported in earlier studies on NMR [23, 24, 32–34].

At temperatures higher than 393 K the isotropic chemical shift continuously increases from $\delta_{iso} = 10$ ppm to approximately $\delta_{iso} = 20$ ppm. At approximately 433 K, which is the temperature just slightly above the $C2/c$- $\beta \rightarrow R–3c–\gamma$ transition, it has reached its final value of approximately 21 ppm. In regime III (433 K to 473 K) a symmetric line is observed, which at temperatures as high as 453 K has almost reached its final width (extreme motional narrowing regime).

Importantly, already at temperatures as low as 373 K a Lorentzian-shaped $^{23}$Na NMR line is seen. This shape points to an almost full averaging of the electric quadrupolar interactions governing the spectra in the rigid-lattice regime at low $T$. For comparison, the $^{23}$Na NMR spin-lattice relaxation rate $R_1$ passes through a maximum at $T_{max} = 393$ K; the corresponding rate peak is shown in figure 5(C) and (D). According to the condition $\omega_0\tau_\gamma \approx 1$, which is valid at the peak maximum, we estimated that the motional correlation rate $1/\tau_c$ for Na-ion dynamics is given by $1/\tau_c = 4.9 \times 10^8$ s$^{-1}$, 1/$\tau_c$ is, within a factor of 2, identical with the jump rate $1/\tau_f$. Using the Einstein-Smoluchowski equation $D = \overline{\ell} (2d\tau_f)^{-1}$, with $\overline{\ell}$ denoting the jump distance (herein, between M1 and M2), and $d$ being the dimensionality of the diffusion process, this translates, with $d = 3$, into a self-diffusion coefficient of $9.0 \times 10^{-12}$ m$^2$ s$^{-1}$ at 393 K. With the help of the Nernst–Einstein equation (see above) we estimate that our results from NMR would correspond to an ion conductivity of $2.4 \times 10^{-2}$ S cm$^{-1}$ at 393 K. These values are in excellent agreement with those obtained by impedance spectroscopy. Thus, at least the position of the NMR rate peak reflects the same dynamic behavior as seen by electrical relaxation experiments.

To see whether $^{23}$Na also yields similar activation energies we used a modified BPP-type spectral density function $J(\omega) \propto R_1$ to analyze the full relaxation peak whose flanks entail information on $E_a$. Importantly, the $R_1(1/T)$ rate peak is asymmetric in shape and points to correlated or length-scale dependent motion.

Originally, Bloembergen, Purcell and Pound used a Lorentzian-shaped spectral density function $J(\omega) \propto \tau_f/(1 + (\omega_0\tau_c)^2)$, where $\beta$ represents the asymmetry parameter [36, 37]. $1 < \beta \leq 2$ allows for a sub-quadratic dependence of the spin–lattice relaxation rate on frequency. Such a dependence produces asymmetric rate peaks. Here, $\beta$ turned out to be 1.55. Whereas local jump processes are probed in the regime $\omega_0\tau_c > 1$, long-range ion transport in NSP is detected if $\omega_0\tau_c < 1$, i.e., at temperatures higher than $T_{max}$. In this regime $^{23}$Na NMR is sensitive to ion transport, which is characterized by an activation energy of $E_{a,high–T} = 0.36$ eV, if temperatures ranging from 393 K to 473 K are considered. This value is in good agreement with the activation energy $E_{a,bulk}$ obtained by impedance spectroscopy. Below 393 K, that is, in the limit where only few jump events are detected during one Larmor precession, we see that local Na-ion dynamics are to be characterized by $E_{a,low–T} = 0.19$ eV. This value agrees with earlier reports on similar compounds [38]. In general, the two activation energies obey the well-known relationship $E_{a,low–T} = (\beta - 1)E_{a,high–T}$ [39], which is also fulfilled here. Interestingly, the $^{23}$Na NMR lines reveal further line narrowing above $T_{max} = 393$ K. Hence, an additional, but much slower diffusion process than that seen by the $R_1(1/T)$ peak is expected at elevated temperatures. Presumably, Na-ion diffusion involving sites along the [001] pathway might be involved in this slower diffusion process.

### 3.6. Ion diffusion as seen by AIMD

We also studied ion dynamics in NSP by AIMD simulations. Since the diffusion coefficient obtained by AIMD represents self-diffusion, it can directly be compared to values obtained by NMR. In general, the tracer diffusion coefficient $D_{tracer}$ is linked to the self-diffusion $D_{id}$ coefficient by a correlation factor, $D_{tracer} = fD_{id}$. On the other hand, the solid-state diffusion coefficient obtained by impedance spectroscopy is connected to $D_{tracer}$ via $D_{tracer} = H_4D$, where $H_4$ denotes the Haven ratio [40, 41]. Only for uncorrelated motion we would expect $f = 1$.

The temperature dependence of the calculated diffusion coefficients $D_{AIMD}$ together with the isosurface of the Na-ion probability density from AIMD simulations are illustrated in figure 5(E) and (F).

$D_{AIMD}$ follows Arrhenius behavior according to $D_{AIMD} = A \exp(-E_{a,AIMD}/(k_BT))$ with $E_{a,AIMD} = 0.18$ eV. To compare the results from AIMD calculations with those from $^{23}$Na NMR spin–lattice relaxation and impedance spectroscopy we extrapolated the Arrhenius line down to 393 K. In table 3 the results are summarized. It turned out that the diffusion coefficients agree with each other within an order of magnitude. As an example, the diffusion coefficients obtained from AIMD and NMR are $9.1 \times 10^{-12}$ m$^2$ s$^{-1}$ and $9.0 \times 10^{-12}$ m$^2$ s$^{-1}$, respectively.
Along the anisotropic lattice expansion, which opens the bottlenecks solely along energies, Na-ion transport properties along both orientations fully merge towards higher temperatures. This temperature ionic transport in the crystallizes in SG C2\textsubscript{1}M3Sc\textsubscript{2}PO\textsubscript{4}.

Here, we studied the dependence of ionic transport on crystal orientation of NaSICON-type materials. In excellent agreement with values obtained by impedance spectroscopy, the high-conductivities in NaSICON-type ceramics for battery applications.

The difference in diffusion coefficients seen by AIMD on the one hand and \textsuperscript{23}Na NMR (and impedance spectroscopy) on the other hand presumably reflects the fact that AIMD does not take into account Na-ion ordering, which influences Na-ion dynamics at lower temperatures. Additionally, the AIMD simulations do not result in any difference between ion transport along [001] and [100]. Accordingly, the corresponding activation energies (0.18 eV) are quite similar. They are, however, much smaller than those seen by impedance spectroscopy (0.40 eV, 0.43 eV). The lower mean activation energy of 0.18 eV calculated could again be explained by dynamic processes, which are not captured by the AIMD simulations.

On the other hand, the activation energy derived from simulations agrees very well with that seen by \textsuperscript{23}Na NMR. This similarity could be related to Na-ion ordering, which only affects the Na-ion transport perpendicular to the [001] direction (see above). Thus, we conclude that the activation energy, which we extracted from the low-T flank of the NMR R\textsubscript{1}(1/T), indeed characterizes local jump processes that seem to be not affected by Na\textsuperscript{+} ordering. In excellent agreement with values obtained by impedance spectroscopy, the high-T flank of the R\textsubscript{1}(1/T) rate peak is, however, sensitive to long-range Na\textsuperscript{+} transport (0.37 eV) containing both the features of long-range ion transport and short-range processes.

### 4. Conclusions

Here, we studied the dependence of ionic transport on crystal orientation of NaSICON-type flux-grown M\textsubscript{3}Sc\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} (M = Na, Ag) single crystals with well-defined facets. At room temperature Na\textsubscript{3}Sc\textsubscript{2}(PO\textsubscript{4})\textsubscript{3} crystallizes in SG C2\textsubscript{1}/c-\beta. At 423 K it undergoes a phase transition to SG R\textsubscript{3}c-\gamma. We found that at ambient temperature ionic transport in the C2\textsubscript{1}/c-\beta regime along the orientation [001] is slightly higher compared to that along the [100] direction. The lower activation energy probed by impedance spectroscopy is related to anisotropic lattice expansion, which opens the bottlenecks solely along [100]. Because of the different activation energies, Na-ion transport properties along both orientations fully merge towards higher temperatures. This behavior leads to isotropic Na-ion diffusion, which is directly related to the order-disorder phase transition from C2\textsubscript{1}/c-\beta \rightarrow R\textsubscript{3}c-\gamma. This phase transition is associated with an increasingly hindered thermal motion of Na\textsuperscript{+} along [001]. This hindering is caused by an increasing jump distance along the lattice expanding direction.

The exchange of Na\textsuperscript{+} by Ag\textsuperscript{+} leads to the stabilization of the R\textsubscript{3}c-\gamma phase at RT. In contrast to Na\textsubscript{3}Sc\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}, we observed two phase transitions for Ag\textsubscript{3}Sc\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}, taking place at 289 K and 180 K; they represent the following changes in space groups C2\textsubscript{1}/c-\beta \rightarrow R\textsubscript{3}c-\gamma and a C2\textsubscript{1}/c-\beta \rightarrow C2\textsubscript{1}/c.-\alpha.

Interestingly, ionic conductivities follow a similar Arrhenius behavior as seen for Na\textsubscript{3}Sc\textsubscript{2}(PO\textsubscript{4})\textsubscript{3}, but shifts to lower temperatures. The stabilization of the R\textsubscript{3}c-\gamma at lower temperature could be related to the different side occupation behavior and higher mobility of Ag\textsuperscript{+} compared to Na\textsuperscript{+} leading to isotropic diffusion at much lower temperatures.

In summary, we showed that the phase transition behavior of NaSICON-type materials is linked to ionic diffusion and vice versa. Ionic transport depends on bottleneck sizes and on the site occupation behavior of the mobile charge carriers. We expect that small compositional changes may significantly affect these properties; thus, it is not unexpected that a broad distribution of dynamic parameters is reported in literature for powdered samples. Considering the suggested interrelations between bottleneck sizes, changes in lattice parameters and diffusion pathways, well thought-out crystal chemical engineering represents the key to maximize ionic conductivities in NaSICON-type ceramics for battery applications.

| Method     | D/10^{-12} m\textsuperscript{2} s\textsuperscript{-1} (at 393 K) | E\textsubscript{a}/eV |
|------------|-------------------------------------------------------------|----------------------|
|            | [100] | [001] | [100] | [001] |                   |                  |
| AIMD       | 86   | 95   | 0.18  | 0.17  |                   |                  |
| average    | 91   | short range: 0.19 long range: 0.37 | 0.18 | 0.40  | 0.43  |                  |
| impedance  | 6.5  | 6.4  | 0.40  | 0.43  |                   |                  |
| average    | 6.5  |       |       |       |                   |                  |

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Acknowledgments

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Conflicts of interest

There are no conflicts to declare.

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