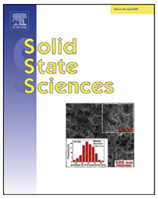
Solid State Sciences 67 (2017) 30–36

Contents lists available at ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie



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

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ARTICLE INFO

Article history:
Received 22 September 2016
Received in revised form
7 March 2017
Accepted 11 March 2017
Available online 14 March 2017

Keywords:
Neutron diffraction
NASICON
Crystal structure
Ionic conductivity

ABSTRACT

A study of the series $Na_{3+x}Sc_2Si_xP_{3-x}O_{12}$ ($0 < x < 0.8$) 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 $Na_{3.4}Sc_2Si_{0.4}P_{2.6}O_{12}$ 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 $Na_3Sc_2P_3O_{12}$ 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 [3–5]. In order to understand the high conductivity in this class of ceramic electrolyte materials, a compositional guideline for high ionic conduction was 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 mol 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 Ref. [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.

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http://dx.doi.org/10.1016/j.solidstatesciences.2017.03.005

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 und 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 Å) with the centre wavelength of 1.333 Å. 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

3.1. Le Bail profile fitting

The profile fitting was carried out using the refined unit cell parameters obtained from the XRD pattern of $Na_{3.4}Sc_2Si_{0.4}P_{2.6}O_{12}$, which showed only one rhombohedral phase with space group $R\overline{3}c$ and less than 3% of a monoclinic phase with space group $\frac{C2}{c}$, a structural subgroup of the first phase [8]. However, the refinement of the profile parameters of the neutron diffraction data with space group $R\overline{3}c$ 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.

3.2. 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.

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: $Na_3Sc_2P_3O_{12}$ for the monoclinic phase and $Na_{3.8}Sc_2Si_{0.8}P_{2.2}O_{12}$ 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 Fig. 1. Atomic parameters and equivalent displacement parameters are given in Table 2 and Table 3, respectively.

4. Discussion

4.1. 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 $Na_3Sc_2(PO_4)_3$, 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.

4.2. Ordering of Na ions and pathway for the Na conduction

The pathways of Na^+ ions in both the rhombohedral and