Experimental report

15/04/2024

Proposal: 5-22-807 **Council:** 10/2022

Title: Phase analyses of Na ion-conducting glass-ceramic composites

Research area: Materials

This proposal is a new proposal

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Samples: Na3,4Zr2Si2,4P0,6O12
Na3.4Zr1.85Si2.45P0.68O11.99
Na3.4Zr1.7Si2.5P0.75O11.98
Na3.4Zr1.55Si2.55P0.83O11.96
Na3.4Zr1.4Si2.6P0.9O11.95
Na3.4Zr1.85Si2.35P0.65O11.73
Na3.4Zr1.7Si2.3P0.7O11.45
Na3.4Zr1.55Si2.25P0.75O11.18
Na3.4Zr1.4Si2.2P0.8O10.90

Instrument	Requested days	Allocated days	From	To
D20	1	1	25/05/2023	26/05/2023
D2B	1	0		
D22	1	0		

Abstract:

NaSICON-type compounds with the general composition Na1+xZr2SixP3-xO12 are again more intensively investigated for battery applications. In an attempt to better understand the phase formation of NaSICON compositions with Zr deficiency, we are exploring two series of compositions, both with an increasing Zr deficiency, but with stoichiometric and excess of (P + Si) content. The proposed experiments shall primarily elucidate the final compositional variation in the crystalline phase along the two series. Additional information on the formed glassy phase would be very helpful to understand the whole system. The quantification of the glassy phase and its constituents is important to understand the chemical equilibria at high temperatures. The X-ray atomic scattering factors of light atoms (here Na and O) are very low and Si and P have only one electron difference, which makes an accurate determination of the final crystalline NaSICON compositions impossible by XRD technique.

Experimental report for proposal 5-22-807
Phase analyses of Na ion-conducting glass-ceramic composites

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Introduction
NaSICON-type materials show high Na^+ ionic conductivity in range of 1-5 mS/cm at room temperature [1,2]. So far 5 mS/cm is one of the highest ionic conductivities known so far [3]. In an attempt to better understand the phase formation of NaSICON compositions with Zr deficiency, we have explored the systems $Na_{3.4}Zr_{2-3x/4}Si_{2.4-x/4}P_{0.6+x/4}O_{12-11x/8}$ and $Na_{3.4}Zr_{2-3x/4}Si_{2.4+x/4}P_{0.6+1.5x/4}O_{12-x/16}$ ($0<x<0.8$), both with an increasing Zr deficiency, but with stoichiometric and excess of (P + Si) content, respectively. In addition, the nominal amount of O^{2-} vacancies is changing significantly between the two series. These series show promising ionic conductivity and high density at relative low sintering temperatures compared with those of the conventional NaSICON materials $Na_{3+x}Zr_2Si_{2+x}P_{1-x}O_{12}$. The proposed experiments shall primarily elucidate the final compositional variation in the crystalline phase along the two series.

Experimental
neutron diffraction (ND) study was performed on powders at the high-flux two-axis D20 beam line at ILL. A take-off angle of 118 ° from the Ge(117) monochromator (λ ~ 1.3581 Å) was chosen and each measurement was carried out for 45 minutes at 295 K with position-sensitive detectors spanning from 2° to 160° angular range with steps of 0.1°. Vanadium cylinders of 5 mm in diameter were filled with powder of eight NZSP samples (~1.2 g each) and measured at room-temperature The Rietveld refinements were carried out using the Thompson-Cox-Hastings pseudo-Voigt peak shape function, implemented in the software package Fullprof Suite [4,5]. The diffraction background was interpolated between manually set points. Lattice parameters, zero-point shifts and peak shapes were initially refined using the Le Bail method. During the final cycles of the refinement, the occupancy factors for mixed occupied Si/P sites were constrained to add up to full occupation. Their thermal displacement and position parameters were constrained to be equal. The thermal displacement parameters and site occupation factors (SOF) of Na, Si/P atoms were refined in alternating cycles until convergence was reached (< 0.1 % difference between cycles) and fixed at the last cycle to result in a final stoichiometry.
A high-temperature ND study of one of the powders failed due to decomposition in the vanadium cylinder.

Results
As a starting model for Rietveld refinement the crystal structures of both known phases of NaSICON-type materials were used, the monoclinic (*C2/c*) and rhombohedral ($R\bar{3}c$) polymorphs. In the case of the single rhombohedral phase, the wR_p values varied between 4.5 % and 7.1 %. In the single monoclinic phase and the two-phase mixture, values were in range of 2.1 % to 3.1 % and 2.3 % to 6.94 %, respectively. Based on these wR_p values and the previous XRD results, the main phase in all samples was refined as monoclinic NaSICON phase. In addition, the diffractograms contain few weak reflections of minority phases. Further analyses of these weak additional reflections showed that the minority phase can be

Table 1. Lattice parameters, phase fractions and residual values of refinements for the NaSICON samples determined by ND

Series	x	Refined composition	a / Å	b / Å	c / Å	β / °	V / Å^3	NaSICON fraction / %	Impurity	wR_2, wR_p
1 + 2	0	$Na_{3.62}Zr_{1.95}Si_{2.4}P_{0.6}O_{12}$	15.7859(4)	9.1241(2)	9.2126(2)	124.4(1)	1095.14(5)	98(1)	ZrO_2	2.95, 3.75
1	0.2	$Na_{3.56}Zr_{1.95}Si_{2.35}P_{0.65}O_{12}$	15.7655(5)	9.1142(3)	9.2282(3)	124.2(1)	1096.35(6)	100(1)	-	2.96, 3.84
1	0.4	$Na_{3.58}Zr_{1.93}Si_{2.3}P_{0.7}O_{12}$	15.7741(4)	9.1172(2)	9.2274(2)	124.3(1)	1096.53(5)	83(1)	$Na_3Si_2PO_8$	2.31, 2.98
1	0.6	$Na_{3.47}Zr_{1.95}Si_{2.25}P_{0.75}O_{12}$	15.7499(5)	9.1076(3)	9.2314(3)	124.1(1)	1096.10(6)	90 (1)	$Na_3Si_2PO_8$	2.53, 3.28
1	0.8	$Na_{3.47}Zr_{1.93}Si_{2.2}P_{0.8}O_{12}$	15.7505(5)	9.1081(3)	9.2332(3)	124.1(1)	1096.40(6)	93(1)	$Na_3Si_2PO_8$	2.59, 3.38
2	0.2	$Na_{3.47}Zr_{1.96}Si_{2.32}P_{0.68}O_{12}$	15.7362(3)	9.1008(2)	9.2416(2)	124.0(1)	1097.04(4)	86(4)	$Na_3Si_2PO_8$	2.62, 3.40
2	0.4	$Na_{3.44}Zr_{1.95}Si_{2.25}P_{0.75}O_{12}$	15.7292(4)	9.0976(2)	9.2395(2)	124.0(1)	1096.45(5)	90(1)	$Na_3Si_2PO_8$	2.38, 3.04
2	0.6	n. a.	-	-	-	-	-	-	-	-
2	0.8	$Na_{3.35}Zr_{1.94}Si_{2.1}P_{0.9}O_{12}$	15.7048(5)	9.0845(3)	9.2388(3)	123.9(1)	1094.68(6)	69 (2)	$Na_3Si_2PO_8$	2.30, 3.01

identified as $Na_3Si_2PO_8$ (ISCD 161804) as a crystallization product of the glassy phase. One sample (with x = 0) revealed peaks of ZrO_2 as a secondary phase (**Table 1**).
In a second step of the refinements, all atomic positions for the main and minority phases were refined. In addition, the site occupancy factors (SOF) and thermal displacement parameters (TDP) of oxygen atoms were checked carefully for the main phase. All oxygen atoms showed full occupation with reasonable TDP parameters. Therefore, SOF for oxygen atoms were fixed to be 1. In the next step the TDP for statistically distributed Si and P atoms were considered for two fully occupied atomic sites at *4e* and *8f*. When the TDP for Si/P atoms were constrained to be equal, the refinement of SOF resulted in reasonable values close to those expected from nominal composition. In further cycles of the refinement, the SOF of Si/P sites were therefore fixed to stoichiometries with full occupation.
In this work the occupancies of Zr sites were refined without constraints and always resulted in values less than unity between 0.93 to 0.98 according to the compositions given in Table 3. A mixed Zr/Na occupancy of the Zr site as described earlier [6] did not significantly change TDP and resulted in slightly increased wR_p values of up to 4.5 %.
No significant variation was obtained for the averaged bond lengths and they do not show a significant tendency related to the variation of the elements. Therefore, the crystal structure and also the composition of the crystalline phase do not vary much, indicating a stable two-phase region in the investigated area of the phase diagram. The inter-ionic distances also agree very well with those determined from previous structure refinements with similar compositions, either with or without Zr deficiency.
The results of this study are part of an extended publication currently under review.

Crystallographic data files of this work are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe, Access Structures service, and can be retrieved using the deposition numbers 2294186 (S1+2, x = 0), 2294170 (S1, x = 0.2), 2294185 (S1, x = 0.4), 2294189 (S1, x = 0.6), 2294209 (S1, x = 0.8), 2294143 (S2, x = 0.2), 2294169 (S2, x = 0.4), 2294283 (S2, x = 0.8).

References

[1] Q. Ma, M. Guin, S. Naqash, C.-L. Tsai, F. Tietz, O. Guillon, Chem. Mater., 28 (2016) 4821-4828
[2] S. Naqash, D. Sebold, Tietz, O. Guillon, J. Am Ceram. Soc., 102 (2019) 1057-1070
[3] Q. Ma, C.-L. Tsai, X.-K. Wei, M. Heggen, F. Tietz, J. Irvine, J. Mater. Chem. A, 7 (2019) 7766-7776
[4] J. Rodriguez-Carvajal, Physica B: Condens. Matter 192 (1993) 55-69
[5] J. Rodriguez-Carvajal, Commission on Powder Diffraction (IUCr). Newsletter 26 (2001) 12-19
[6] P. R. Rudolf, M. A. Subramanian, A. Clearfield, J. D. Jorgensen, Mater. Res. Bull. 20 (1985) 643-651