NASICON SOLID ELECTROLYTES
PART II - X-RAY DIFFRACTION EXPERIMENTS ON SODIUM-ZIRCONIUM-PHOSPHATE
SINGLE CRYSTALS AT 295K AND AT 993K

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ABSTRACT: The structure of an end member (x=0) of the NASICON solid solution
system $Na_{1+x+4y}Zr_{2-y}Si_xP_{3-x}O_{12}$, $0 \leq x \leq 3$, $0 \leq y \leq 1$ has been investigated
at room temperature and at 993K. At room temperature the NASICON
framework shows static disorder: interstitial sites inside the
ZrO_6-coordination octahedron and split oxygen sites. We present a
model which prompts that both effects are correlated. The occupancy
of the Na2 site - not significant at room temperature - was refined
to about 10% at 993K. The results from both measurements can be
correlated only, if at room temperature Na^+ is located in the in-
terstitial sites and if the transition of these ions to the Na2
site occurs at high temperature. Additional refinement of higher
order temperature coefficients of the Na sites at 993K yielded a Na
diffusion path Na1-Na2 similar to that found in other NASICON com-
positions. The height of the effective one particle potential bar-
rier agrees quite well with the activation enthalpy measured on
single crystals with impedance methods (part III). Therefore we
conclude that in this NASICON composition the main diffusion pro-
cess is a bulk process.
MATERIALS INDEX: NASICON, binary phosphates

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Introduction

Earlier structure investigations on the NASICON solid solution system (1,2) yielded the following composition formula: $Na_{1+x+4y}Zr_{2-y}Si_xP_{3-x}O_{12}$; $0 \leq x \leq 3$, $0 \leq y \leq 1$. Here we report on structure investigations of an end member (x=0). Hagman and Kierkegaard (3) and Hong (4) carried out the first room temperature structure investigations on the NASICON composition $NaZr_2P_3O_{12}$ and - different from all the other structures of NASICON compositions investigated up to now - reported a structure model with only one sodium site (Na1 in FIG. 1). The temperature factor of this site is rather high and this was interpreted as a hint for the mobility of the Na ions (4). This assumption agrees with the noticeable high ionic conductivity recently measured on our crystals (part III)). However, if this conductivity exclusively corresponds to a diffusion mechanism of the Na ions along a path similar to that described in the NASICON compositions x=1.4, y=0.2 and x=3 (part I), a significant occupancy of the Na2 site (FIG. 1) must be expected in contrast to the structure models reported in (3,4). On the other hand, this ionic conductivity may be based on a non bulk diffusion process (e.g. diffusion along domain walls, as found for the composition x=3 (part III)).

By single crystal diffraction experiments at high temperatures combined with ac conductivity measurements we can decide wether the bulk or the domain wall diffusion model is valid: If the bulk diffusion process is the main one and if the temperature is high enough, the diffusion path should be describable with the propability density function of the Na ions ($PDF_{Na}(\vec{r})$). In this case the barrier height of the effective one particle potential derived from this function should agree with the activation enthalpy measured with the impedance technique.

Experimental

The crystals were grown by O. Melnikov $^+$). As starting materials were used: 15g NASICON powder (prepared corresponding to the method of von Alpen et al. (5), the composition is unknown), 77.5g $NaPO_3$, 25g NaCl and 10g NaF. After mixing, these products were heated up to T=1349K and then cooled down to 1069K with a rate of 1.8°/h. The final products are SiO_2 crystals (β-Tridymit) and NASICON crystals. ICP (Inductive Coupled Plasma) and microprobe chemical analyses were carried out to check the Si concentration in these NASICON crystals. No significant Si content was found. This result is in agreement with the lattice parameters determined on single crystals: at room temperature we found a=b= 8.813(3)A and c=22.80(1)A. These values agree quite well with the lattice parameters of $NaZr_2P_3O_{12}$ reported in (3,4).
The single crystal X-ray diffraction experiments were carried out on a Philips PW 1100 diffractometer (step scan method, Mok_{α} radiation). For the measurements at room temperature and at 993K different crystals of the same run were used. The reflection statistics are given in TABLE 1.

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TABLE I: Reflection Statistics and final Fitting

Temp. [K]	numb. of refl. measured	number of unrel. reflections	number of unrel. refl. $I/\sigma(I) \geq 3$	R_i %	$(\frac{\sin\theta}{\lambda})_{max}$ [Å⁻¹]	R_w/R %	GoF
295	2489	876	695	4.0	0.81	2.1/1.6	2.6
993	2028	701	576	3.8	0.75	1.8/2.0	2.3

Table II: Final Atomic Parameters

	Temp. [K]	occup.	$x(\sigma)$	$y(\sigma)$	$z(\sigma)$	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	B [Å²]
Na1	295	1.00(1)+)	0	0	0	.0167(4)	β_{11}	.00031(3)	$\beta_{11}/2$	0	0	2.8
	993	1.00(1)	0	0	0	.122(3)		.00155(9)				20.0
Zr	295	.913(2)	0	0	.14566(1)	.00238(3)	β_{11}	.00214(3)	$\beta_{11}/2$	0	0	0.5
	993	.916(2)			.14697(1)	.00674(4)		.000677(5)				1.5
P	295	1.	.29169(5)	0	1/4	.00131(5)	.00162(6)	.000170(6)	$\beta_{22}/2$	$\beta_{23}/2$	.00019(2)	0.3
	993		.28909(6)			.00541(7)	.00695(9)	.000741(8)			.00071(2)	1.4
O1	295	1.	.1939(1)	.1701(1)	.08752(7)	.0031(3)	.0033(1)	.00041(1)	.0007(2)	.00022(4)	.00026(4)	.9
	993	1.	.1974(4)	.1721(3)	.0917(1)	.0092(2)	.0112(3)	.0159(3)	.0021(2)	.00113(6)	.00100(7)	3.0
O2	295	1.	.1847(2)	-.0166(2)	.19489(5)	.0045(2)	.0056(2)	.00052(2)	.0028(1)	-.00056(7)	.00022(5)	1.1
	993		.1759(4)	-.0288(3)	.19678(7)	.0158(3)	.0193(4)	.0161(3)	.0109(3)	-.00163(8)	.00042(8)	3.7
Na2	295	(0.02(1))	---	---	---	---						---
	993	0.10(3)	-.377(6)	0	1/4	.060(6)	.20(2)	.08(1)	$\beta_{22}/2$	$\beta_{23}/2$	.06(1)	73.0
Zr*	295	.0055(6)	.057(3)	.096(2)	.151(1)	---	---	---	---	---	---	2.0
Zr+	295	.0042(6)	.097(8)	.038(7)	.139(2)	---	---	---	---	---	---	1.7

+) We fixed the Na1-occupancy at 1.00 because when the refinement was tried, we got non realistic values of about 1.01.

Structure Investigations

A detailed description of the general NASICON structure is given in (3,4,6). ZrO_6-octahedra share corners with PO_4^- or SiO_4^--tetrahedra (FIG. 1). Between two ZrO_6-octahedra the Na1-site is located in a destorted octahedron of
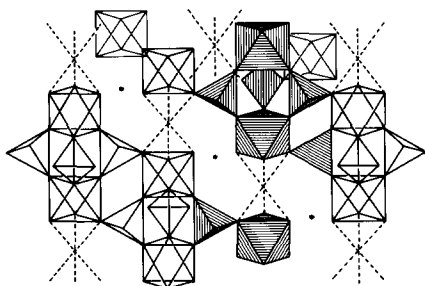

FIG. 1

Part of the NASICON structure in a simplifying figure. The framework is built up of ZrO_6-octahedra which share corners with $(Si,P)O_4$-tetrahedra. To give a better impression from the framework some parts are hatched. The Na1-site lies in the intersection point of the (---) lines and * roughly gives the position of the Na2-site.

oxygen atoms. A second Na site (Na2, in FIG. 1 signed as *) is coordinated by a wide cage of 8 oxygen atoms. This site is thought to be unoccupied in $NaZr_2P_3O_{12}$ (3,4).

The refinement of the structure was started with the room temperature diffraction data and with the structure model published in (4). Refining the occupancy of the Zr site and only anisotropic temperature factors we attained $R_w(F)/R(F)=0.024/0.021$. However, difference Fourier maps showed 6 quite high residual electron density peaks in the vicinity of the Zr-site ($\Delta e \leq 1.2e/A^3$), always three are symmetry related. Several models (e.g. anharmonic temperature factors, different split-models of the Zr-site) were tried to describe these densities. All models, except one failed: In addition to the regular Zr- site, symmetrically independant interstitial sites Zr* and Zr$^+$ were introduced. Now the residual density reduced to $\Delta e \leq 0.4e/A^3$ and the fitting of the structure model improved to $R_w(F)/R(F)=0.021/0.016$. The final atomic parameters are given in TABLE II. The refinement of the split sites was carried out using the scattering factor of Zr^{4+} and isotropic temperature factors. At this point we want to stress that it was not really possible to determine the element occupying these sites. Microprobe analyses gave no hints to any impurities and therefore essentially only Zr or Na are imaginable in these sites. However, with respect to the larger ion size of Na^+ (compared with Zr^{4+}) it seems less probable that Na^+ occupies these interstitial sites because they are not located in the center of the coordination octahedron (TABLE II). From this point of view the assumption of Zr interstitial sites seems to be more reasonable. Therefore in a first model we assume that the Zr-interstitial sites are produced by Na^+ - Zr^{4+} - repulsion, when the Na2-site is occupied. The other way around according to this correlation the occupancy of the Na2-site can be estimated to about 2% from the refined interstitial-occupancies. However, this Na2- occupancy is too low to be recorded with difference Fourier maps.

No matter, which element finally occupies the interstitial sites, the proba-

bility density functions (pdfs) of the oxygen sites suggest that these inter-
stitials are correlated with an oxygen static disorder: The corresponding
$pdf_O(\vec{r})$, which include 3rd and 4th order temperature coefficients (7), are
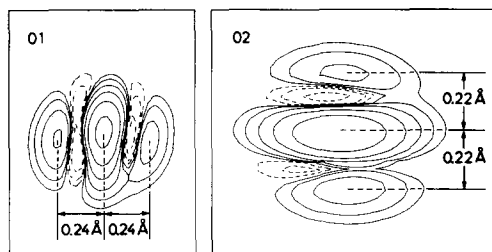given in FIG.2 *). Both pdfs are split, but in different crystallographic

FIG. 2
$pdf_O(\vec{r})$, given in a logarithmic scale
($\pm exp(x)$, $x=2,3,...$). The physically
senseless negative values are plotted
as dashed lines. The c-axis approxi-
mately lies in the figure plane pa-
rallel the margin.

directions. This splitting is quite different to the splitting of the O2-site
found in the NASICON composition x=1.4,y=0.2 (companion paper part I). Sur-
prisingly both pdfs show two additional nonequivalent split sites. This is a
quite significant effect which lead to the following model: If one of the
interstitials is occupied, the three nearest neighbour oxygens of the coordi-
nation octahedron move apart. Each of these shifts is transferred to the
symmetrically equivalent oxygen site of the common PO_4-tetrahedron. In this
way a second non equivalent split site is produced.

At T=993K no static disorder of the framework was found. The refinement was
started with anisotropic temperature factors for all sites. A fit of
$R_w(F)/R(F)=0.019/0.020$ were attained when the Na1 site and the oxygen sites
were refined with additional higher order temperature factor coefficients
(TABLE III). At this state of refinement the Na2 site was introduced. Because
the Na2-site is special, only $x(\sigma)$, 4 anisotropic temperature coefficients
and the occupancy had to be refined. The orientation of the Na2-vibration
ellipsoid was found to be similar to the corresponding ellipsoid in the NASI-
CON compositions x=1.4,y=0.2 and x=3, but the quantitative meaning of its
main axes is limited, because β_{33} did not readily converge. The lack of more
high angle diffraction data (limitation was given by the high temperature
equipment) or (not resolved) Na2-split-positions may be the reason for these
difficulties.

In contrast to the investigations at room temperature, where an occupancy of
the Na2 site cannot.be proven, we found a significant occupancy of about 10%
(TABLE II) but also a fully occupied Na1 site. This means that the lack of Zr
is compensated by additional Na in the Na2 site which yields the following
composition: $Na_{1.3(1)}Zr_{1.832(4)}P_3O_{12}$. The sum of valences is not balanced by
0.3e and therefore the formula was proven with ICP analyses. These gave a
balanced formula $Na_{1.32(3)}Zr_{2.005(6)}P_{2.93(6)}O_{12}$ which confirms the excess of
Na quite well. But the deficiency of P is not really believed.

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*) Here $pdf_O(\vec{r})$ describes static as well as dynamic disorder effects. A
detailed discussion of the meaning of $pdf(\vec{r})$ is given in (8).

Table III: Anharmonic Temperature Factor Coefficients +)

	T=295K		T=993K		
	3rd order	4th order	3rd order	4th order	6th order
Na1	------	------	------	d_{1113} -.008(4) d_{1123} -.021(4) d_{1133} .0021(4)	f_{111111} -.6(1)
P	c_{111} .0007(2) c_{112} .0004(1)	d_{1113} -.00004(2) d_{2233} -.000016(9)			
O1	c_{111} .0007(2) c_{333} .00005(2) c_{112} .0008(4) c_{122} .0006(3) c_{113} .0002(1) c_{223} .0002(1)	d_{1111} .0014(6) d_{1112} .0006(2)	c_{111} .004(1) c_{333} .00027(4) c_{112} .0017(5) c_{113} .008(2) c_{133} .0023(7) c_{223} .005(2)	d_{1111} .0018(6) d_{1122} -.0006(4) d_{1223} -.00028(8) d_{2223} -.0004(1)	
O2	c_{333} -.00003(2) c_{133} -.00008(4) c_{223} -.0002(2)	d_{1333} .00002(1)	c_{111} -.007(2) c_{112} -.005(1) c_{122} -.0032(9) c_{113} .0005(2)	d_{3333} .000023(8) d_{1113} .0008(1) d_{2223} .00028(15) d_{2233} -.00010(5) d_{2333} -.00004(2)	

+) the coefficients of the third, forth and sixth order have to be multiplied by 10^3, 10^4 and 10^6, respectively.
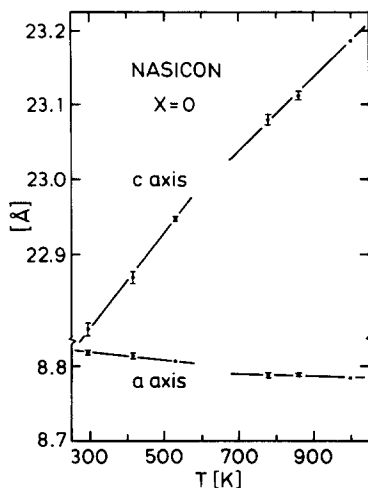
The findings that the static disorder effects of the NASICON framework disappear and the Na2-occupancy changes somewhere between room temperature and 993K gave rise to prove if this behaviour is reflected in a discontinuity of the lattice constants with temperature. The results are given in FIG. 3. It seems that a slight discontinuity takes place somewhere between 550K and 750K.

FIG. 3

Lattice constants of a NASICON endmember (x=0) as a function of temperature (where no error bar is given, it is less than the size of the point).

Na Diffusion Path and Effective One Particle Potential

From the Fourier transform of the temperature factor coefficients of both Na sites we calculated $PDF_{Na}(\vec{r})$ corresponding to the method described in (8). Only at 993K the mobility of the Na^+ was high enough to describe the diffu-
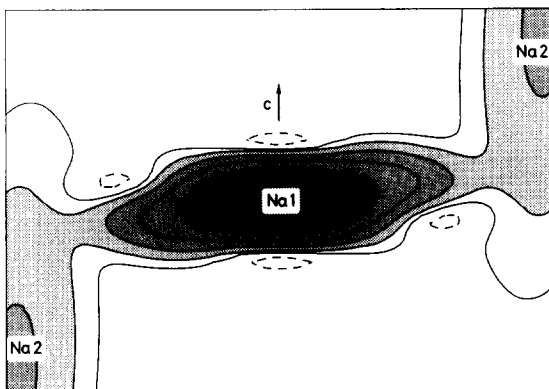

FIG. 4

Diffusion path of the sodium ions at T=993K. Lines of constant probability density are plotted (ln-scaling: ±exp (x), x=2,3,...). The physically senseless values are plotted as dashed lines.

sion path with this function (FIG. 4). It is similar to that in the NASICON compositions x=1.4,y=0.2 and x=3 (for comparison see companion paper part I). The corresponding one particle potential was calculated along the path and is given in FIG. 5. It includes a potential barrier of $\Delta E_{x=0}$=0.37(5)eV. This value is in noticeable good agreement with the activation enthalpy found with ac-conductivity measurements on single crystals of the same charge (see the following paper).
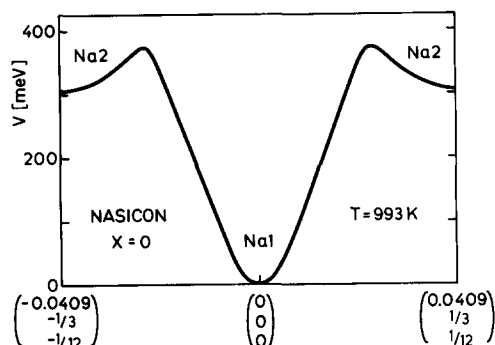
FIG. 5

Effective one particle potential $V_{Na}(\vec{r})$ calculated along the diffusion path.

Summary and Discussion

Refining the room temperature data of an end member (x=0) of the NASICON solid solution system we found a residual electron density inside the coordination octahedron. The structure model significantly improved when two symmetrically independent interstitials were introduced. Probably these interstitials are correlated with the split positions of the oxygens. With elastic X-ray diffraction experiments it is not possible to determine the element occuppying the interstitials, but comparing these results with the measurement at 993K one gets some indirect arguments to assume Na^+ (instead of Zr^{4+}) in the interstitial sites at room temperature:

Firstly, at high temperature no static disorder effects were found. If Zr^{4+} occupies the interstitial sites at room temperature, an increase of the regular Zr-occupancy has to be expected at high temperature. This is not the case (TABLE II). Instead, an increase of the Na2-occupancy was found. Therefore we deduce, that the Na2-occupancy increases with temperature at the expense of the interstitial sites' occupancy because the Na1-site is fully occupied at both temperatures.

Secondly, if Na^+ is assumed in the interstitial sites the occupancies (Table II) have to be multiplied by a factor 4 (corresponding to the lower electron number of Na^+ compared with Zr^{4+}). Considering this model we get the same composition of the crystal at both temperatures: $Na_{1.3(1)}Zr_{1.832(4)}P_3O_{12}$ and therefore we assume that this second model is the right one despite of some objections given above. However, our structure investigation yields a non balanced sum of valences. Interestingly, from all NASICON structure refinements carried out up to now only the structure investigation of the extremely small crystal reported in (2) lead to balanced valances but did not show any extinction effects. May be that the extinction correction of these data here and of the diffraction experiments on the composition x=3 is not good enough although the extinction model of Becker and Coppens (general case) was refined (9).

From the data set measured at 993K we got new results about the diffusion

properties. The Na diffusion path was described and the effective one-particle potential along the path was calculated. From these results we draw the following conclusions:

- As already suggested (10) the diffusion path connects both Na sites and forms a three dimensional network. This has been proven now for three different NASICON compositions and therefore probably can be generalized for the whole NASICON solid solution system.
- The height of the potential barrier $\Delta E = 0.37(5)eV$ agrees with the activation enthalpy found with impedance conductivity measurements (see part III). Therefore we conclude, that the diffusion process in this NASICON composition (x=0) is a pure bulk process.

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