

STRUCTURAL INVESTIGATIONS OF NASICON ( $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ;  $x=3$ )  
WITH X-RAY DIFFRACTION AT 298K AND 403K

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Dedicated to Prof. A. Rabenau on the occasion of his 60th birthday.

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ABSTRACT

Structure investigations on the pure Si end phase of NASICON ( $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ;  $x=3$ ) yielded an underoccupation of the Zr-site. The charge is not balanced by additional Na ions because all regular Na sites are nearly fully occupied and no additional Na site has been found. Infrared spectra show O-H defects in the structure. It is assumed that these defects can balance the charge. The thermal vibrations of the Na sites are both anisotropic and largely temperature dependent with anharmonic contributions at high temperature.

Introduction

NASICON ( $\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$ ;  $0 < x < 3$ ) is one of the technologically important ionic conductors which is considered for application in solid state Na/S batteries (1). At 300°C NASICON has a high Na conductivity of roughly  $2 \times 10^{-1} \text{ (ohm cm)}^{-1}$  in the compositional range  $1.8 < x < 2.5$  (2). The structure of NASICON is related to the garnet structure (3). It consists of a rigid network of (Si,P)  $\text{O}_4$  tetrahedra sharing corners with  $\text{ZrO}_6$  octahedra. Charge balance is established by Na ions located at two sites. In the chain ( $\text{ZrO}_6\text{-Na(1)-ZrO}_6\text{-ZrO}_6\text{-Na(1)-}$ ) with all cations located on the threefold axis parallel c and on a site lying between the chains and coordinated by 6 oxygen atoms ( $\text{Na(2) - O} = 2.53 - 2.67 \text{ \AA}$  and 4 additional oxygens with a longer bondlength  $\text{Na(2) - O} = 3.04 - 3.29 \text{ \AA}$ , at room temperature). This site is assumed to lie on the conduction path (4).

Experimental

Single crystals of NASICON were grown in a platinum crucible by the flux method. Starting compounds were  $\text{NaPO}_3$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$  and  $\text{Na}_2\text{CO}_3$ , the flux consisted of  $\text{NaF}$  and  $\text{V}_2\text{O}_5$ . The mixture reacted in a temperature range of 992–774°C. The data sets were measured on a single crystal of size 0.19 x 0.17 x 0.12 mm<sup>3</sup> at room temperature and at  $T = 403\text{K}$  using a Philips PW 1100 diffractometer (stepscan method,  $\text{Mo K}\alpha$  radiation). The measurements were carried out assuming monoclinic symmetry and the structure refinement was started on the basis of the monoclinic structure model of Hong (5). However, after analysing all reflections as well as the refined structural parameters the monoclinic space group ( $\text{C2/c}$ ) was dropped in favour of a rhombohedral space group ( $\text{R}\bar{3}\text{c}$ ). Photographs of the reciprocal lattice with the precession method confirmed the higher symmetry. At room temperature no diffuse intensity was observed. For refinement of the rhombohedral structure two data sets with 481 ( $\theta < 30^\circ$ ; RT) and 687 ( $\theta < 34^\circ$ ;  $T = 403\text{K}$ ) symmetry unrelated reflections have been used. The final structure refinements resulted in the weighted R values of  $R_w = 0.02$  (RT) and  $R_w = 0.018$  ( $T = 403\text{K}$ ). Final positional parameters and lattice constants are listed in Table I.

TABLE I  
Atomic Positional Parameters and Cell Constants

		x( $\sigma$ )	y( $\sigma$ )	z( $\sigma$ )
Na(1)	298K	.0	.0	.0
	403K	.0	.0	.0
Na(2)	298K	-.3617(1)	.0	.25
	403K	-.3611(1)	.0	.25
Zr	298K	.0	.0	.14675(1)
	403K	.0	.0	.14696(1)
Si	298K	.29688(7)	.0	.25
	403K	.29649(5)	.0	.25
O(1)	298K	.1855(2)	.1666(1)	.08495(5)
	403K	.1859(1)	.1663(1)	.08541(4)
O(2)	298K	.1842(1)	-.0172(2)	.19124(6)
	403K	.1838(1)	-.0184(1)	.19128(5)

## Cell Constants at 298K and 403K

	a	c
298K	9.186(6)	22.186(7)
403K	9.193(6)	22.289(7)

ICP (Inductive Coupled Plasma) and microprobe chemical analyses were done to check for any occupation of the (Si,P) sites by phosphor. No significant phosphor content has been found.

Results and discussion

The bond lengths ((Si,P) - O(1) = 1.619(2)Å and (Si,P) - O(2) = 1.621(2)Å) obtained from the room temperature data set confirm that the pure Si end phase of the NASICON system has been investigated.

According to the composition proposed for NASICON (5) it is then expected that all sites are fully occupied. This is in disagreement with the following results: The Na(2) site seems to be fully occupied (.99(1)), however, the Na(1) site shows an occupation of only .970(7). Furthermore, the Zr site is underoccupied; the refinements resulted in a value of only .905(3). Na(1) shows large, isotropic thermal vibrations in the (a,b) - plane and a significantly smaller RMS amplitude perpendicular to it. Na(2) vibrates very anisotropically, with the largest amplitude pointing nearly into the c direction (Table II). The 298K data have been refined only with harmonic, but anisotropic temperature factors. For the refinement of the 403K data anharmonic temperature factors (6) have been used up to third order for Na(2) and up to fourth order for Na(1). Significant anharmonic contributions were found. About  $.7\text{\AA}$  from the Zr site in  $\pm c$  direction significant residual electron density with a maximum of about  $1e/\text{\AA}^3$  has been found by difference Fourier analyses in both data sets. This density may have different reasons:

- anharmonicity of the Zr potential in the c direction
- the Zr site is split.

Therefore anharmonic temperature factors up to the fourth order were applied to the Zr site for the high temperature data set. A significant decrease of the residual electron density and an improvement of the R-value ( $R_w = .015$ ) occurred. But measurements at still higher temperatures should be carried out to allow the selection of the best model.

TABLE II

Mean Axes of the Vibration Ellipsoids of the Sodium Ions and their Orientation to Crystallographic Axes

Temp.	Site	RMS-amplitude $\text{\AA}$	Orientation ( $^\circ$ ) referred to crystallographic axes		
			a	b	c
298K	Na(1)	.089(5)	90	90	0
		.168(4)	120	00	90
		.168(4)	210	90	90
	Na(2)	.115(3)	90	147	76
		.158(2)	180	60	90
		.251(2)	90	78	13
403K	Na(1)	.089(3)	90	90	0
		.202(2)	120	0	90
		.202(3)	210	90	90
	Na(2)	.110(2)	90	148	78
		.154(2)	180	60	90
		.285(1)	90	80	12

Due to the underoccupation of the Zr site the charge is not balanced. Compensation can be achieved by the addition of more cations or by partial substitution of the oxygens through monovalent anions. The difference Fourier analyses did not reveal any additional cationic sites in the structure. An infrared spectrum was made from powdered

single crystals (Fig. 1); it shows absorption bands at  $500 - 600 \text{ cm}^{-1}$  and  $850 - 1000 \text{ cm}^{-1}$ . These are attributed to  $\text{SiO}_4$  stretching and bending vibrations. The sharp double band at about  $2900 \text{ cm}^{-1}$  is a C - H absorption band and is due to the experimental set up. But the rather broad absorption band between  $3300 \text{ cm}^{-1}$  and  $3600 \text{ cm}^{-1}$  is typical for O - H vibrations. As there is no significant absorption band at about  $1600 \text{ cm}^{-1}$  where one would expect a vibration frequency of water, we conclude that the observed vibration band is with high probability caused by O - H defects in the crystal structure; this kind of defects is well known in natural quartz (7).

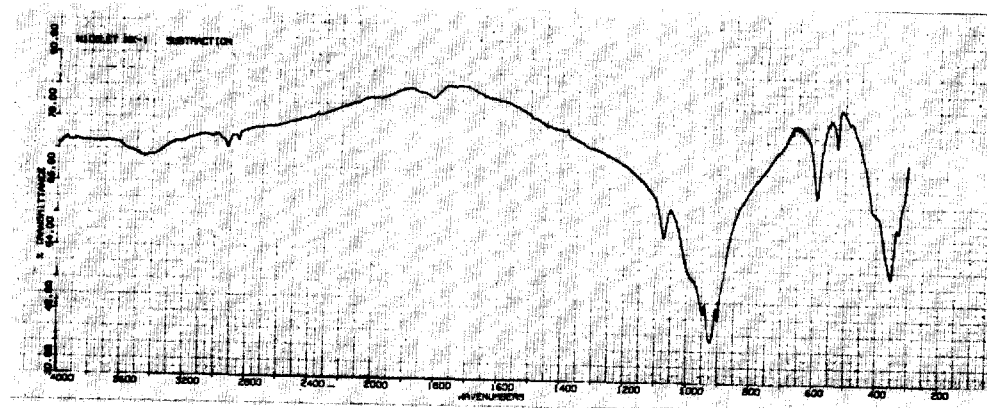


FIG. 1

Infrared spectrum of the pure Si end phase of NASICON

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