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Hydrothermal synthesis and structural investigation of sodium zirconium silicophosphates

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The hydrothermal reactions of $NaZr_2(PO_4)_3$ with Na_2SiO_3 in excess NaOH at 300 °C have been investigated. The pure precursor phases have been obtained at the reactant ratio of $NaZr_2(PO_4)_3 : Na_2SiO_3$ from 1 : 1 to 1 : 3.2. When the reactant ratio reached 1 : 3.5 in the case of a large excess of NaOH, $Na_4Zr_2(SiO_4)_3$ was obtained. The structures of the precursor phases were studied by X-ray diffraction, infrared and magic angle spinning nuclear magnetic resonance spectroscopy. The results showed that these NASICON-like phases were similar to 6.06 phase designated by Clearfield *et al.*, which were converted into sodium zirconium silicophosphates on heating to 1000 °C. All NASICON phases prepared by this process were pure phases and free ZrO_2 remained. The structure and ionic conductivity of these NASICONs have been investigated and the results compared with literature data. The compounds in some of the range of composition appear to have a maximum ionic conductivity at 300 °C (0.2 Ω^{-1} cm^{-1}). This method provides a very effective and convenient route for preparing all compounds in the NASICON family.

1. Introduction

Sodium zirconium silicophosphates (NASICON) with the general formula $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leqslant x \leqslant 3$) exhibit, for some compositions, a good three-dimensional ionic conductivity and have considerable chemical and thermal stabilities [1]. Thus, the materials have been widely investigated because of their potential uses. NASICON compounds have an open three-dimensional skeleton framework of PO_4 and SiO_4 tetrahedra corner-shared with ZrO_6 octahedra. One end-member of the NASICON series is a pure phosphate, $NaZr_2(PO_4)_3$, and the other end-member is a pure silicate, $Na_4Zr_2(SiO_4)_3$. The compounds between two end-members are, respectively, formed with the different substitutions of SiO_4 for PO_4 in the structure of $NaZr_2(PO_4)_3$.

The sodium zirconium silicophosphates are generally prepared by solid-state reactions at high temperature [1]. Recent studies have shown that it is extremely difficult to prepare a single phase by this method [2], because some ZrO_2 remains and glassy silicate phases formed at high temperature were present in the final products [3]. This lowers the conductivity by producing a high intergrain resistance. Therefore, it is desirable to develop a synthesis method that does not suffer from these shortcomings. In recent years, the hydrothermal method has been developed for synthesizing phosphate ionic conductors, due to the low *PT*-conditions for crystallization [4, 5]. Clearfield *et al.* [6] reported the hydrothermal preparation of NASICON compounds by reacting $Zr(HPO_4)_2 \cdot H_2O$ with Na_4SiO_4. They achieved a hydrated phase, which on heating to 1200° C yielded NASICON phase.

Recently, we systematically studied the synthesis of NASICON-type compounds under hydrothermal conditions and obtained $NaZr_2(PO_4)_3$ (NZP) [7]. Because sodium zirconium silicophosphates could be prepared by partial substitution of silicon for phosphorus in $NaZr_2(PO_4)_3$ under conditions of constant zirconium content, the reactions of NZP with Na_2SiO_3 in excess NaOH under hydrothermal conditions were investigated. A precursor phase was obtained, which converted into NASICON on heating to ~1000° C. The hydrothermal processes, structural investigation of the products by X-ray, infrared, magic angle spinning nuclear magnetic resonance techniques and the ionic conductivities of the samples are described in detail in this paper.

2. Experimental procedure

2.1. Synthesis procedure

A highly crystalline $NaZr_2(PO_4)_3$ was prepared by the hydrothermal method. $ZrOCl_2 \cdot 8H_2O$, H_3PO_4 (85%) and NaOH solution were mixed in the autoclave with

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a Teflon liner, which was heated at 250 °C. The crystallinity of $NaZr_2(PO_4)_3$ was examined by X-ray powder diffraction.

The hydrothermal reaction of NZP with Na_2SiO_3 was carried out in a stainless steel autoclave with a Teflon liner. $Na_2SiO_3 \cdot 9H_2O$ was accurately weighed and dissolved in deionized water in the Teflon liner. NZP was weighed accurately, and NaOH was then added. The autoclaves were heated to 290–300 °C in an oven for varying lengths of time. Filling levels were of the order of 60%, so that the autoclave pressures were approximately 12.1 mPa. The recovered solid was washed and dried in air.

2.2. X-ray diffraction

The X-ray powder diffraction (XRD) patterns of all the samples obtained in the experiments were taken using a Rigaku D/MAX-III A diffractometer with CuK_α radiation ($\lambda = 0.154\ 18$ nm). Using a least-squares programme, the lattice parameters of the samples were calculated.

2.3. Infrared spectroscopy

The infrared spectra of the samples were recorded in the range 1400– 400 cm^{-1} with a 5DX spectrometer by the conventional pressed-disc method (KBr discs).

2.4. Ionic conductivity

The ionic conductivity of the samples was measured by the complex impedance method from room temperature to 300 °C with a ZL5-type precise LCR bridge in the frequency range 12 Hz–100 kHz.

The powder samples were cold-pressed into pellets (10 mm diameter, ~2–3 mm thick) under a pressure of about 3 T cm^{-2}. The pellets were sintered at 1000–1100 °C for 10 h, and polished. The faces were coated with silver by the vacuum evaporation technique. The coated pellet was placed between two silver-blocking electrodes for the measurements.

3. Results

The results of a number of hydrothermal reactions of NZP with Na_2SiO_3 in varying proportions are presented in Table I. All products were pure phases in the ratio NZP : Na_2SiO_3 from 1:1.0 to 1:3.2. The XRD patterns of these phases were similar to those of the 6.06 phase designated by Clearfield *et al.* [8] (the number designates the first interplanar spacing (Å) in its X-ray diffraction pattern). When the ratio of NZP : Na_2SiO_3 was 1:3.5 in the case of a large excess of NaOH, $Na_4Zr_2(SiO_4)_3$ was obtained. This compound is the other end-member of the NASICON series, in which phosphorus is completely replaced by silicon. We felt that the following reactions could occur in the hydrothermal system

$$NaZr_2(PO_4) + xNa_2SiO_3 + 2xNaOH \rightarrow$$
$$Na_{1+x}Zr_2Si_xP_{3-x}O_{12} + xNa_3PO_4 + xH_2O \quad (0 \leqslant x \leqslant 3) \qquad (1)$$

TABLE I. Results of hydrothermally reacting NZP with Na_2SiO_3 at 300 °C

Experiment	Reactant Ratio NZP:Na_2SiO_3 (mol)	Concentration NaOH (mol l^{-1})	Time (d)	Phases formed
Y-110	1:1.0	1.2	3	6.06
Y-111	1:1.5	1.3	3	6.06
Y-113	1:2	1.4	3	6.06
Y-114	1:2.5	1.5	3	6.06
Y-115	1:3	1.7	3	6.06
Y-117	1:3.2	2.1	4	6.06
Y-121	1:3.5	5	5	$Na_4Zr_2(SiO_4)_3$

TABLE II. Unit cell parameters of 6.06 phases

Sample	NZP : Na_2SiO_3 (mol)	*a* (nm)	*b* (nm)	*c* (nm)
Y-110	1:1.0	0.8722	1.0285	0.7293
Y-111	1:1.5	0.8735	1.0311	0.7303
Y-113	1:2.0	0.8756	1.0454	0.7321
Y-115	1:3.0	0.8808	1.0563	0.7342
Y-117	1:3.2	0.8854	1.0707	0.7457

From Table I, it is seen that the amounts of Na_2SiO_3 and NaOH were in excess in the experiments.

The results of ^{31}P, ^{29}Si NMR showed that the content of phosphorus increased with decreasing silicon in the filtrate after the reaction. Therefore, the reaction of NZP with Na_2SiO_3 under hydrothermal conditions is deduced to be a substitution reaction, in which silicon will replace phosphorus under conditions of constant zirconium content. Thus, the substitution of silicon for phosphorus in the hydrothermal reactions may be controlled by the Na_2SiO_3 and NaOH content, so that partial or complete substitutions were obtained after the reactions.

In another experiment, the 6.06 phase was reacted with 6M HCl at 300 °C in an autoclave. The product was a rhombohedral proton-form of NZP. Therefore, Reaction 1 is reversible under hydrothermal conditions and the framework structure of NZP undergoes no change during the reactions.

For all 6.06 phases, the XRD patterns appeared similar, but their *d*-spacings showed a slight shift as the ratio of NZP : Na_2SiO_3 changed during the reactions. The XRD data of the 6.06 phases were indexed on the basis of an orthorhombic cell, and the results are given in Table II. From the increase in the lattice parameters, it is evident that the silicon content in these phases increased with the ratio of NZP : Na_2SiO_3 from 1:1.0 to 1:3.2.

Fig. 1 shows infrared spectra for samples of different compositions. With increasing silicon content, the main absorption bands in the spectra shifted gradually from 1100 cm^{-1} to 980 cm^{-1}, which were assigned to PO_4 and SiO_4 bending and stretching vibrations, respectively [9]. This is in agreement with the results of the lattice parameters.

The high-temperature NASICON phases were formed on heating the 6.06 phases in air at ~1000 ° C.

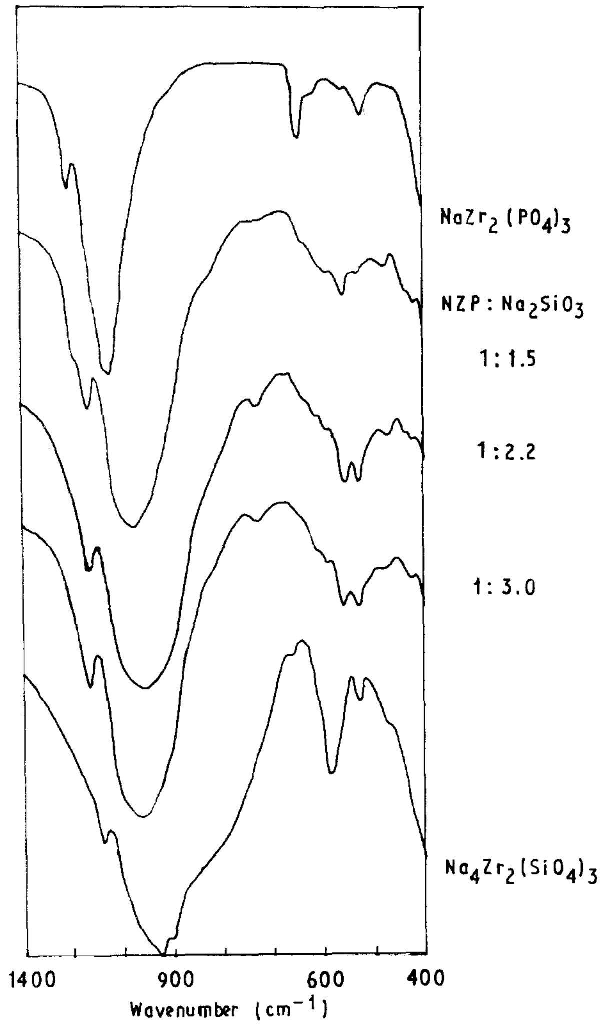

Figure 1 Infrared spectra of the 6.06 phases for different compositions.

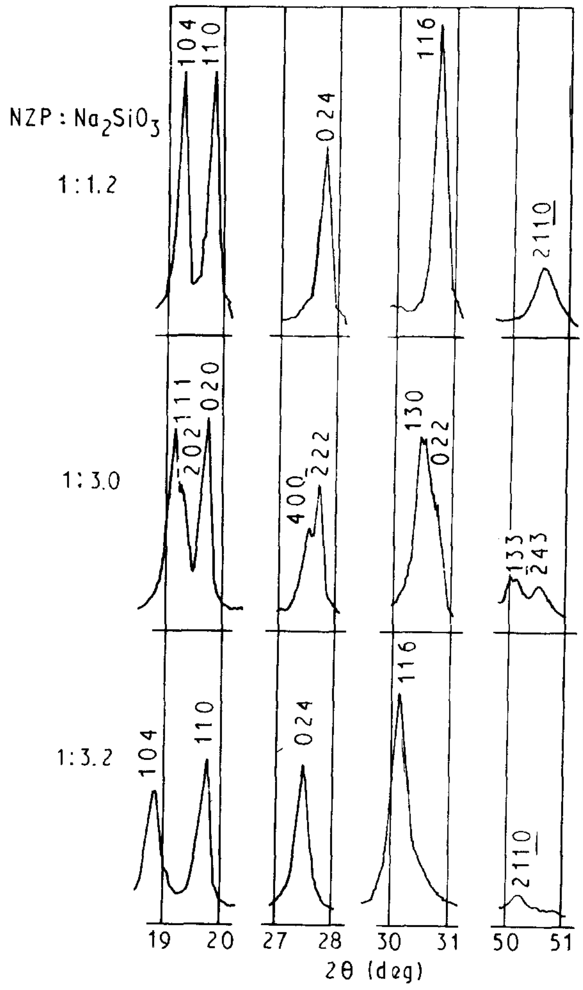

Figure 2 X-ray diffraction patterns of NASICONs in various compositions at room temperature.

A conversion of the structure occurred during the heating process. The XRD patterns of these high-temperature phases were identical to those of NASICON compounds obtained by solid-state reactions [10] but were free of ZrO_2 and other impurities. These X-ray powder diagrams were presented in our previous work [11].

In NASICON series compounds, $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ ($0 \leqslant x \leqslant 3$), a structural transition between a phase with a monoclinic symmetry and one with a rhombohedral symmetry occurred with composition x at room temperature [10]. In our experiment, the XRD patterns of high-temperature phases with different compositions were recorded at room temperature (Fig. 2). Pattern modifications with changing composition were observed. The single peaks with Miller indices 1 0 4, 1 1 0, 0 2 4, 1 1 6, 2 1 1 0, corresponding to NZP:Na_2SiO_3 = 1 : 1.0 to 1 : 2.0, which are characteristic peaks of rhombohedral structural symmetry, occur in split form in the ratio range = 2.2–3.0, which are characteristic of monoclinic structural symmetry. All split peaks changed to single peaks when the ratio of reactants exceeded 1 : 3.0. This result showed that all compounds of various compositions (x = 1–3) in NASICON series can be prepared by our hydrothermal process.

From the results of infrared spectroscopy and ^{31}P, ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR) for high-temperature phases, it was proved that NASICON compounds obtained from this method are neither glassy phase nor other condensed phosphates and silicates. The results of ^{31}P, ^{29}Si MAS NMR on these compounds will be published elsewhere.

Measurement of ionic conductivity for samples of various compositions was carried out at different temperatures. The ionic conductivity data showed that all NASICON compounds prepared by this method behave like fast-ion conductors. The conductivity value reached a maximum 0.2 Ω^{-1} cm^{-1} at 300 °C for the sample obtained from the reactant ratio of NZP : Na_2SiO_3 = 1 : 3.0. This is in good agreement with the results of Goodenough *et al.* [12] Conductivities of the samples were also obtained from impedance measurements. Fig. 3 shows a typical admittance plot for the highest conducting composition (ratio = 1 : 3) at three different temperatures. The plots show the characteristic features commonly observed for ceramic solid electrolytes [13] when measurements are made with blocking electrodes.

4. Conclusions

This study has shown that it is possible to prepare NASICON-like phases hydrothermally, which convert to NASICON compounds at 1000 °C. A new

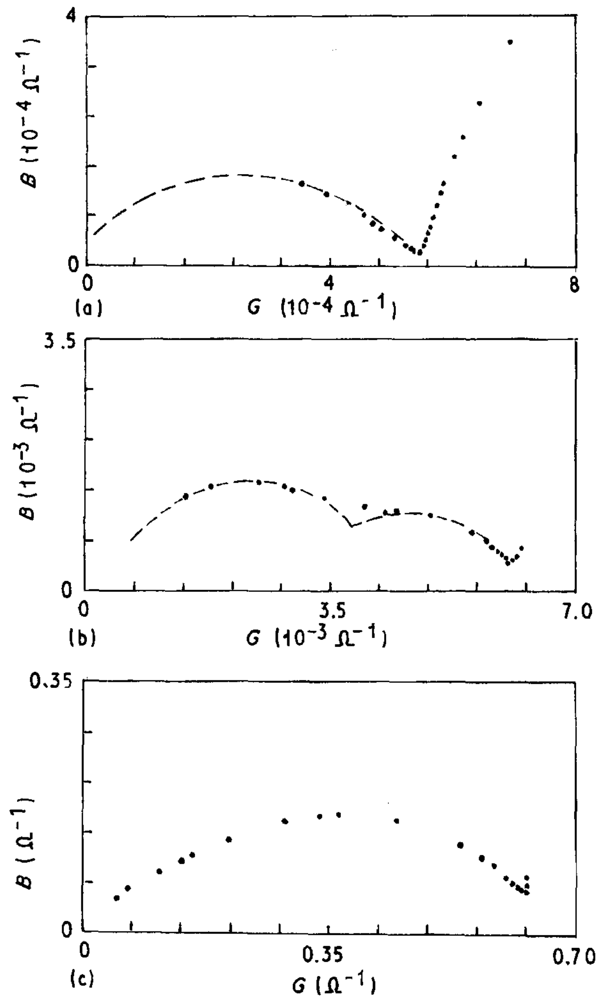

Figure 3 Admittance diagram of NASICON for the highest conducting composition at different temperatures: (a) 25 °C, (b) 80 °C, (c) 300 °C.

route has also been found for preparing NASICON series compounds. The hydrothermally prepared NASICONs remained as a single phase even on heating to a high temperature, and these compounds appear to have good ionic conductivity. By hydrothermal reaction, two end-members in the NASICON series, $NaZr_2(PO_4)_3$ and $Na_4Zr_2(SiO_4)_3$, as well as all members between them, are found to be related. This is very important for investigating all compounds in the NASICON family. Our study is more progressive than that of Clearfield *et al.* and suggests the possibility of preparing directly a pure sodium zirconium silicophosphates.

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