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Short communication

Structural studies of NASICON material of different compositions by sol–gel method

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Abstract

The NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) is a well known solid electrolyte material with high ionic conductivity. The ion conductivity can be improved by modifying the structure. The NASICON powders with different compositions (by varying x) have been prepared by sol–gel method. The structural and conductivity measurements have been done by XRD, complex plane impedance analysis and electrochemical cell method. The results indicate that the ac conductivity and Na^+ ion selectivity are higher for $x = 2.05$ as compared to other compositions. The enhancement of Na^+ ion conductivity for $x = 2.05$ has been attributed to modifications in the orientations of tetrahedral structures which lead to change in the bottleneck size. The results have been confirmed by X-ray diffraction (XRD).

Keywords: C. Ionic conductivity; NASICON; Sol–gel

1. Introduction

For the last 30 years, NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) material (acronym for Na SuperIonic CONductors) has been used for gas sensing, Na^+ based batteries and ion selective electrodes because of its high ionic conductivity as compared to other solid electrolyte materials such as sodium beta alumina, cubic stabilized zirconium [1–3]. The high value of ionic conductivity of this group of compounds is an effect of both, high ion charge carrier concentration and high mobility. The high concentration and high mobility of charge carriers of these solid electrolytes are due to the crystal structure of these compounds. The structures of these compounds consist of the two kinds of ions, one constituting the immobile space crystal lattice and the other, easy moving inside this lattice and establishing the molten sub lattice. In general, NASICON has three dimensional frameworks for Na^+ migration [2,4,8]. The mobile ions are generally small size cations, so such type of conductors are called cation conductors. The basic structure of NASICON material is rhombohedral in which two ZrO_6 octahedra are separated by three $(Si,P)O_4$ tetrahedra with which they share corner oxygen atoms and two types of Na sites (Na1 and Na2). The Na1 site is located between two octahedra along the c axis and other site Na2 is at midway of two Na1 sites along the a axis [5,6,9]. The two sodium sites, Na1 and Na2, inside the channels, are connected through triangular bottlenecks of oxygen atoms. The bottleneck between both sites for the rhombohedral symmetry is formed of three oxygen atoms whose centres make up an isosceles triangle (Fig. 1). High ionic conductivity, due to movement of sodium ions, depends upon the size of bottleneck, activation energy required for the movement of ions and lattice parameters whose value can be modified by changing compositions [10]. The bottleneck size is related to the variation in the lattice parameters a and c. By changing x, Si is partially substituting P which in turn modifies the orientation of the tetrahedral. Several researchers have studied the relation between composition, structure and electrical conductivity for different NASICON type materials prepared by ceramic routes [3,7]. The conventional ceramic routes require high sintering temperatures which lead to volatilization of Na and P whereas NASICON powders prepared by sol–gel method require lower temperature and the obtained materials are more dense and homogeneous. Therefore, in the present work, we have synthesized nano grain powders of NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) compounds of different compositions such as $Na_2Zr_2SiP_2O_{12}$ ($x = 1.0$),

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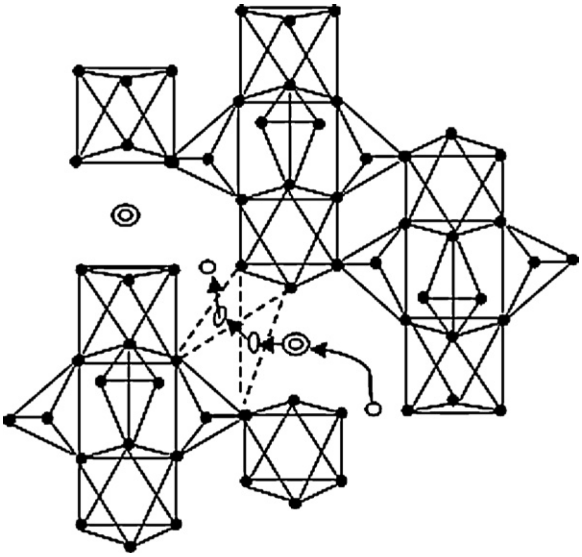

Fig. 1. Schematic representation of NASICON structure. The two sites for Na^+ ions are represented as follows: Na1 by double circles and Na 2 by open circles. Oxygen atoms are represented by closed circles. The bottleneck is shown by dotted lines.

$Na_{3.05}Zr_2Si_{2.05}P_{0.95}O_{12}$ ($x = 2.05$) and $Na_{1.1}Zr_2P_{2.89}Si_{0.11}O_{12}$ ($x = 0.1$) prepared by sol–gel method and studied the effect of x on the structural properties, ac conductivity and Na^+ selectivity in these hot pressed sintered pellets.

2. Experimental techniques

The powders of NASICON ($Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) with $x = 0.1$, 1.0, 2.05, were prepared using a mixed inorganic–organic sol–gel synthesis which involved the preliminary formation of a xerogel [11]. A measured volume of zirconium n-propoxide solution ($Zr(OC_3H_2)_4$) was mixed with distilled water. This solution was then mixed with aqueous solution of NaOH and SiO_2 powders in appropriate ratio. The solution was stirred for 30 min. The calculated amount of aqueous $NH_4H_2PO_4$ was added to previous solution and kept for precipitation. The final precipitate was dried at 150 °C and then sintered at 1000 °C for 3 h. The sintered powder was then pressed in the form of pellets by applying 11 MPa pressure. The pellets were again sintered at 1000 °C for 3 h. In our study, to prepare NASICON powder with various compositions of x, the proper proportion of NaOH, $NH_4H_2PO_4$ and SiO_2 were mixed as needed in order to achieve the proper ratio of Na:Si:P in NASICON.

The structural characterization of powders was carried out by XRD. The XRD patterns were recorded at room temperature by using Philips XPERT-PRO diffractrometer system (2θ range was taken from 10° to 80°) using Cu Kα radiation having a wavelength of 1.5406 Å. The elemental analysis was done by Energy Dispersive X-ray (EDX) technique. The carbon coated samples were used to minimise the charging problem during EDX analysis. The performance of NASICON, sodium ion based sensors, with different compositions of constituent was studied and compared using an electrochemical cell method in which Ag/AgCl electrodes were used. The cell is represented by

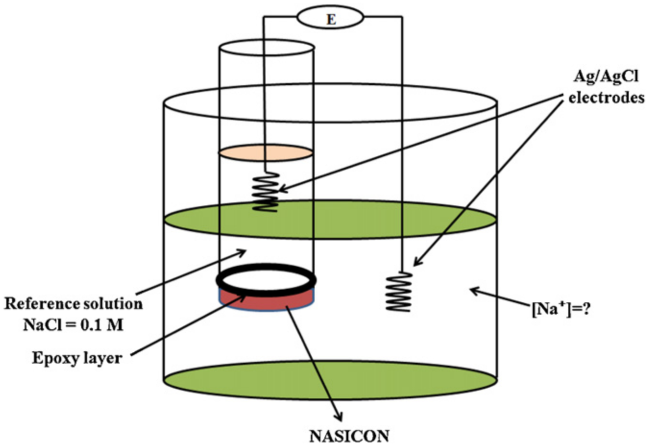

Fig. 2. Schematic representation of the electrochemical cell used for Na^+ concentration measurements.

Ag/AgCl/[ref] NaCl/NASICON/[?] NaCl/AgCl/Ag

where [ref] is the concentration of the reference NaCl solution, which was kept constant and equal to 0.1 M and [?] stands for unknown Na^+ concentration that was to be measured. A schematic diagram is given in Fig. 2. The Ag/AgCl electrodes were made electrochemically by forming an AgCl layer around a silver wire dipped in HCl liquid electrolyte. The emf readings, across electrodes, were taken by using solutions of different molarities. The impedance spectroscopy (complex plane analysis) was used to evaluate the ac conductivity. The measurements were carried out at room temperature in the frequency range 10 Hz to 100 kHz by using HIOKI 3522-50 LCR meter. Silver electrodes were painted on both the surfaces of dense pellets and sintered at 450 °C for 2 h to get good electrical contact.

To measure ac conductivity, impedance spectroscopy (LCR meter) has been used. Silver electrodes were painted on both sides of the samples and sintered at 450 °C for 3 h. It has been ensured that area of the electrode is the effective area of sample only and hence reducing air capacitance. Ac conductivity is given by [13,14]

$$\sigma_{ac} = \omega \xi_0 \xi'' \tag{2.1}$$

where ω is the angular frequency, $\omega = 2\pi f$, ξ_0 is the permittivity of the free space, ξ'' is the imaginary part of dielectric constant as

$$\xi'' = \xi'' \tan\delta \tag{2.2}$$

where $\tan\delta$ is the loss tangent related to the phase angle θ, $\tan\delta = |1/\tan\theta|$, ξ' is the real part of dielectric constant as

$$\xi' = \frac{Cd}{A\xi_0} \tag{2.3}$$

where C is the capacitance, d is the thickness and A is the area of the sample. C and θ are measurable quantities. Then ac conductivity is

$$\sigma_{ac} = 2\pi f \xi_0 \xi' \tan\theta \qquad (2.4)$$

Total impedance for equivalent circuit, as shown in Fig. 7, is given by

$$Z = R_s + \frac{R_p}{1 + (j2\pi f R_p C_p)} \qquad (2.5)$$

real and imaginary part of impedance of the equivalent circuit are given by

$$Z_{re} = R_s + \frac{R_p}{1 + (\omega^2 R_p^2 C_p^2)} \qquad (2.6)$$

and

$$Z_{im} = \frac{R_p^2 C_p \omega}{1 + (\omega^2 R_p^2 C_p^2)} \qquad (2.7)$$

3. Results and discussion

3.1. Structural studies

The elemental analysis of all the samples has been carried out by EDX analysis. The EDX spectra show the presence of Na, Zr, Si, and P along with O and C as given in Fig. 3. The XRD spectra for NASICON compounds with different compositions are shown in Fig. 4. Most of the intense peaks observed in the pattern well match to the peaks in standard JCPDS files of NASICON with corresponding compositions. The average particle size calculated by using Debye–Scherrer formula has been found to be 20 nm in each case. Table 1 shows the lattice parameters and volume of the NASICON for different compositions (calculated from XRD data by using Xpowder ver.2004.04.70 PRO software). As x increases lattice parameters, a and c, show increasing trend. Since the bottleneck size depends on lattice parameters and unit volume, therefore, the maximum increase in the bottleneck size is for $x = 2.05$ as compared to other compositions.

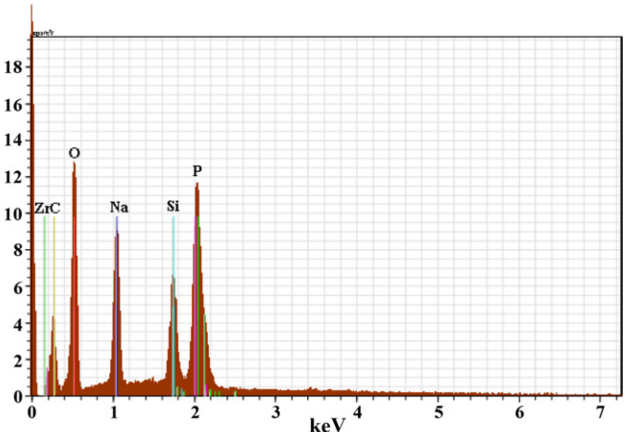

Fig. 3. EDX analysis of the compound $Na_{3.05}Zr_2Si_{2.05}P_{0.95}O_{12}$ ($x = 2.05$).

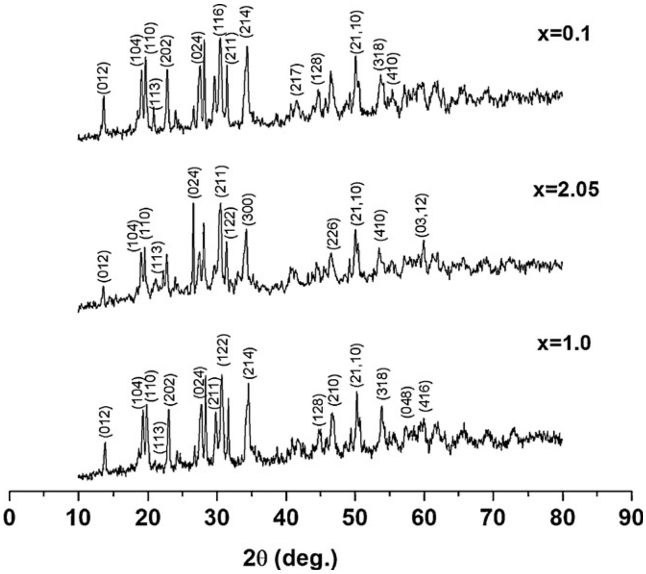

Fig. 4. XRD pattern of NASICON prepared by sol–gel method for x = 1.0, 2.05, 0.1.

3.2. Study of sodium ion (Na^+) concentration of NASICON of different compositions

From electrochemical cell method, the emf values for different NASICON compositions have been measured. By changing the molarity of the solutions (M = 0.1, 0.5, 1.0, 1.5), corresponding induced emf values have been measured after stabilizing both reference and the measured solutions. The emf readings were taken at least 5 min after immersion of the Ag/AgCl electrodes in the solutions. The emf values have been measured at room temperature for NASICON of different compositions and plotted against molarity of different solutions as shown in Fig. 5. It has been found that for $x = 2.05$, the emf value is higher than that of other compositions when measured with solutions of different molarities. It means that Na^+ is more selective for $x = 2.05$. The Na^+ concentration in the unknown solution can be determined by using Nernst equation given below.

By Nernst equation, the emf of the cell is given by

$$E = \frac{RT}{F} \ln \frac{[Na^+]^{ref}[Cl^-]^{ref}\gamma^{ref^2}}{[Na^+]^{?}[Cl^-]^{?}\gamma^{?^2}}$$

where R is the gas constant, F is faraday constant. Superscripts ref and ? denote the values $[Na^+]$ (sodium ion concentration) and γ (mean ionic activity coefficient) at two sides of the cell.

Table 1
Lattice parameters and unit volume for NASICON compounds.

Composition	x	a (nm)	c (nm)	Volume (nm^3)	Structure
$Na_{1.1}Zr_2P_{2.89}Si_{0.11}O_{12}$	0.1	0.8788	2.311	1.54600	Rhombohedral
$Na_2Zr_2SiP_2O_{12}$	1.0	0.8934	2.284	1.57945	Rhombohedral
$Na_{3.05}Zr_2Si_{2.05}P_{0.95}O_{12}$	2.05	0.9068	2.298	1.63645	Rhombohedral

Table 2
Sodium ion concentration for NASICON of different compositions.

Structure	Mean ionic activity coefficient (Y) for molarity 0.1 M [11]	Temperature (T) (°K)	Na^+ concentration ($mol\,l^{-1}$)	Mean ionic activity coefficient (Y) for molarity 1.0 M [11]
$Na_{1.1}Zr_2P_{2.89}Si_{0.11}O_{12}$	0.779	300	0.3609	0.657
$Na_2Zr_2SiP_2O_{12}$	0.779	300	0.4134	0.657
$Na_{3.05}Zr_2Si_{2.05}P_{0.95}O_{12}$	0.779	300	0.5528	0.657

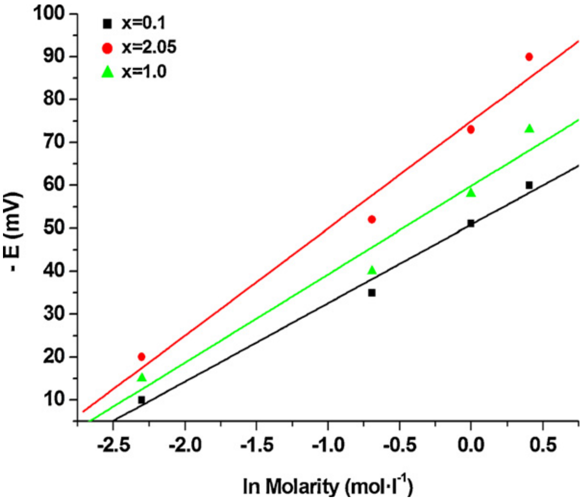

Fig. 5. Emf values of NASICON of different compositions are plotted as a function of molarity of different solutions.

By knowing the value of emf, concentration of reference solution and mean ionic activity coefficient of NaCl [12], the unknown Na^+ concentration has been calculated for all three compositions. Table 2 shows that the sodium ion concentration is higher for the sample having $x = 2.05$ at room temperature.

3.3. Impedance analysis

Complex plane impedance analysis is a well-known and powerful technique, which has long been used for investigating dielectric and semiconducting materials. To analyze and interpret the experimental data, complex plane analysis is the representation of the electrical properties. Fig. 6 shows the Nyquist plot for these three compounds at room temperature in the frequency range 10 Hz to 100 kHz. The semicircles observed in the graphs are not starting from the origin which means that there is a finite resistance (R_s) in series with parallel combination of R_p and C_p. This combination of R and C is the equivalent circuit representation of the sample (Fig. 7). The semicircle can be represented by a parallel RC element and the equivalent circuit consists of a series of array of parallel RC elements attached with a series resistance with constant phase element. Series resistance corresponds to grain resistance whereas grain boundary resistance is represented by a resistance which is attached in parallel to a capacitor. The value of both types of resistances depends upon the structure of the compounds. Ac conductivity for different compositions has been calculated with the help of Eq. (2.7) at 10 kHz and results are given in Table 3. The conductivity has been found to be higher for the composition with $x = 2.05$.

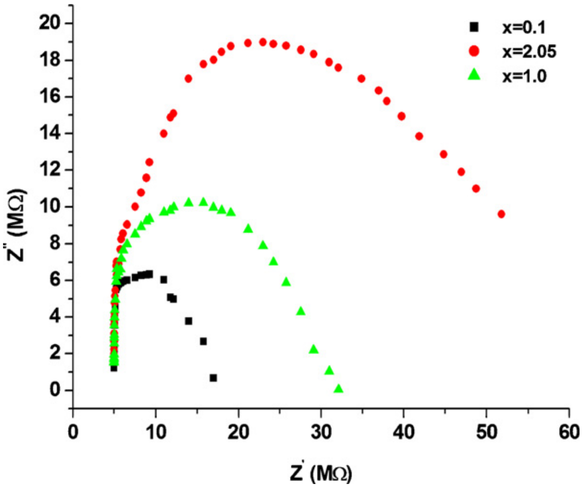

Fig. 6. Impedance spectra at room temperature of NASICON of different compositions.

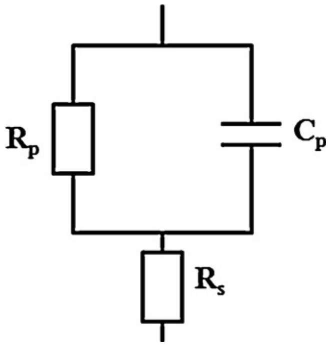

Fig. 7. Equivalent circuit of the samples on the basis of impedance analysis.

Table 3
Capacitance (C_p) and ac conductivity in different compositions at room temperature.

Structure	C_p (pf)	ac conductivity(μS/m)
$Na_{3.05}Zr_2Si_{2.05}P_{0.95}O_{12}$	1.25	2.01
$Na_2Zr_2SiP_2O_{12}$	0.81	1.626
$Na_{1.1}Zr_2P_{2.89}Si_{0.11}O_{12}$	0.565	0.903

4. Conclusions

In summary, nano grain powders (about 20 nm) of NASICON of different compositions have been synthesized. Complex plane impedance analysis reveals that ac conductivity is higher for $x = 2.05$ as compared to other compositions. Using electrochemical cell method, It has been found that the emf produced is higher for the pellet having $x = 2.05$ as compared to other composition which indicate higher Na^+ selectivity for this pellet. XRD data confirms that by increasing x up to 2.05, there is an increase in the values of lattice parameters and unit cell volume which modifies the orientations of tetrahedral structures and hence bottleneck size. Since the a and c (bottleneck size) is found to be maximum for $x = 2.05$, therefore, more conduction crossectional area is available for sodium ion migration as compared to other compositions.

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