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Properties studies on the P-doping NASICON powders

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The development of solid electrolytes has been given a boost by the discovery of the NASICON structure [1, 2]. Crystalline NASICON generally possesses a rhombohedral structure, in which the BO_6 octahedron share corners with the PO_4 tetrahedron and the SiO_4 tetrahedron. NASICON possesses 'open' structures in which alkali ions can move with significantly reduced activation barriers and hence there is potential for applications as fast ion conductors [3, 4].

However, a lot of evaporation of phosphorus occurred during the sintering process. The framework was destroyed, so that the electronical conductivity was decreased [5–7]. It is obvious that the content of phosphorus is important for electronical conductivity and CO_2 response of sensors. In this work we increased the conductivity and sensitivity to CO_2 of NASICON through diffusing P into NASICON disks in order to increase the content of P in samples.

NASICON powders were synthesized by the sol-gel method [8, 9]. The pellets were obtained by applying a pressure of about 14×10^3 kg·cm^{-2} for about 10 min. The doping course was completed in a diffusion system. The $(NH_4)H_2PO_4$ powders used as a source for phosphorus were decomposed at 850 °C. The NASICON pellets were sintered at 550 °C and were doped by incorporating P_2O_5 and P_2O_3.

As shown in Fig. 1, the X-ray diffraction (XRD) patterns of NASICON indicated sharp diffraction peaks signifying a high level of crystallinity. The powders presented better structures and showed small peaks of tetragonal zirconia.

X-ray photoelectronic spectra (XPS) analysis was performed in order to determine the chemical nature of the interfacial layer and the chemical composition of the specimens, as shown in Fig. 2. The binding energies of the Na1s, Zr3d, Si2p, P2p and O1s core level electrons for the $Na_3Zr_2Si_2PO_{12}$ powders before implanting P and after implanting P were determined from the respective XPS and are listed in Table I.

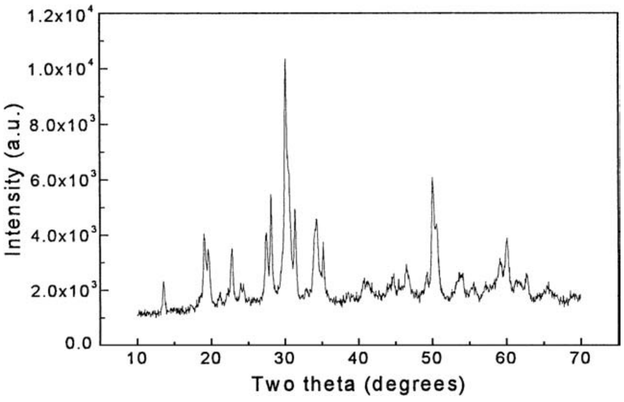

Figure 1 XRD spectra of NASICON powders by the sol-gel method.

Slight variations have been observed for the binding energies of the Zr3d, Si2p, P2p, O1s and Na1s core level electrons for both samples. These variations have been attributed to the changes in the next nearest neighbors of the cation [5]. The framework was varied with the P content. The ratio of elements of the un-doped and doped samples can be obtained approximately. It is revealed by XPS that the P content of the doped sample was more than the un-doped sample.

Complex impedance analysis of the electrical data has been carried out to determine the electrical conductivity of the samples before implanting P and after implanting P. The relevant data are listed in Table II. The higher conductivity was shown by the doped sample. It is known that the conductivity of NASICON

TABLE I XPS core level binding energies of various elements in (a) un-doped disk (b) doped disk in NASICON systems, values are in eV

	Na1s	Zr3d	Si2p	P2p	O1s
(a)	1069.6	181.5	100.8	132.7	531.5
(b)	1069.8	181.6	100.5	132.9	531.0

TABLE II Electrical data of the un-doped disk and doped disk

Sample	$\sigma_{303\ K}$ (S cm^{-1})	E_a (0.01 eV)
Un-doped	8.36×10^{-4}	0.33
Doped	4.05×10^{-3}	0.32

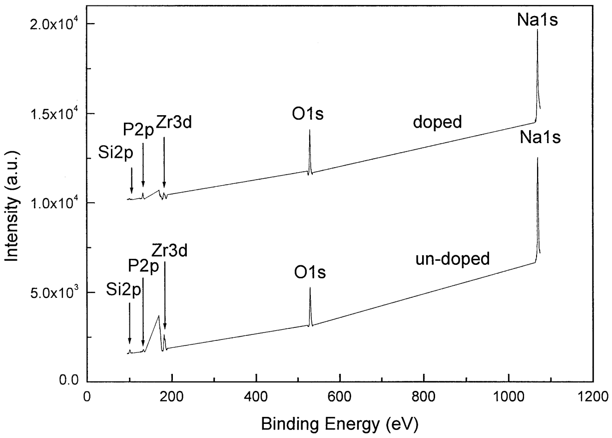

Figure 2 XPS spectrum for doped and un-doped NASICON samples.

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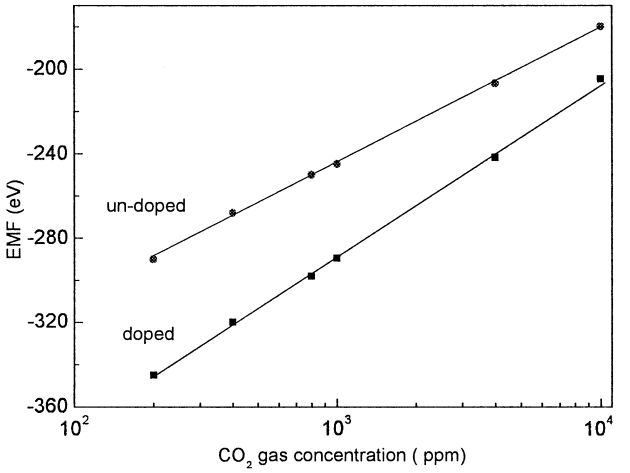

Figure 3 The CO_2 concentration dependence of the EMF for the NASICON samples.

decreases with a decrease in the lattice constants because of a decrement of the runnel size for Na^+ migration [10]. It is obvious that the doped powders have the better framework in their structure due to the higher P content.

Fig. 3 shows the relationship between the EMF response and the CO_2 gas concentration for the gas sensors prepared using the samples. For the sensor using the doped powder, the measured sensitivity of 71.5 mV/decade was close to the theoretical value of 74.0 mV/decade based on a two-electron electrochemical reaction [11]. In the case of the sensor using the un-doped powder, the sensitivity was 66.3 mV/decade.

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