Sol–gel synthesis of NASICON discs from aqueous solution

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Sodium superionic conductor (NASICON: $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$) discs of high density and relatively high purity can be easily synthesized with good reproducibility by a sol–gel method using a mixed solution of inorganic materials, by evaporation, calcination, and sintering. The densities and ionic conductivities of the NASICON discs were largely dependent on the calcination and sintering conditions, the optimum temperatures of which were found to be 750 °C (1 h) and 1000 °C (6 h), respectively. It was also found that high-density and relatively high-purity NASICON discs could be derived more easily by controlling the pH of the sol in the first step to *ca.* 3.0.

Sodium zirconium silicophosphate with the NASICON-type structure is known as one of the best solid-state sodium conductors for applications in solid-state electrochemical devices, such as gas sensors,[1,2] ion sensors,[3,4] and high-energy-density batteries. So far, NASICON samples have been usually prepared from conventional solid-state reactions at temperatures >1200 °C.[5–8] Whereas high-density NASICON discs were obtained from these processes, the high-temperature reactions readily led to secondary phases such as monoclinic zirconia,[8] as well as to volatilization of Na_2O and P_2O_5 from the samples. Thus, low-temperature processes such as sol–gel methods would be preferable to produce high-purity (without ZrO_2 phase) NASICON samples. So far, sol–gel processes using metal alkoxides,[9–15] citrates,[8,16] silicates (silica gel),[9,17–19] and zirconium hydrogen phosphate[9,20,21] have been reported in the synthesis of NASICON samples. Well crystallized and fine NASICON powders were obtained at relatively low temperatures but sintering at high temperatures of *ca.* 1200–1350 °C was still required to obtain high-density NASICON discs. Recently, we found that well crystallized and relatively high-purity NASICON powders and discs could be prepared by a far simpler sol–gel process starting from aqueous solutions of inorganic materials at relatively low temperatures of between 850 and 1000 °C.[22] However, the NASICON discs obtained were too porous to fabricate an electrochemical cell. In further investigations, it was revealed that high-density and relatively high-purity NASICON discs could be synthesized at relatively low temperature by controlling the synthetic conditions of the sol–gel route. This study deals with the conditions of the sol–gel process to prepare NASICON sintered discs with high density and the properties of these discs.

Experimental

NASICON ($Na_3Zr_2Si_2PO_{12}$) was synthesized by the sol–gel (silica gel) method[15,22] using all-aqueous solutions as shown in Fig. 1. Solutions of $ZrO(NO_3)_2 \cdot 8H_2O$, $NH_4H_2PO_4$ and $Na_2SiO_3 \cdot 9H_2O$ (2 : 1 : 2 in molar ratio; Na in excess of stoichiometric composition[22]) were mixed together to form a sol, which was further dehydrated at 60 °C for *ca.* 3 h to form a viscous gel. In some cases, the pH of the sol was adjusted with HNO_3 and/or $(NH_4)_2HPO_4$. The gel was then dried at 110 °C for 12 h to form a fine dry xerogel powder, which was then ground and calcined at 650–850 °C for 1 h. The calcined material was reground and pressed into sample discs (diameter 12 mm, thickness 1 mm) under 500 MPa, and then finally sintered at 950–1050 °C for 6 h in air. The products were characterized with X-ray diffractometry (XRD) (XD-D1, Shimadzu Ltd.), thermogravimetric (TG)–differential thermal analysis (DTA) (TG–DTA 200, Seiko Instruments Inc.), and X-ray fluorescence analysis (XRF, Rigaku Denki 3270). The surface morphology was examined by scanning electron microscopy (SEM, JEOL, JSM-840F). Densities of the NASICON discs were calculated from their mass and dimensions. The ionic conductivity was measured with an impedance analyser (HP-4800A, Hewlett Packard; 5–500 kHz) using Au-coated discs at 20–90 °C.

Results and Discussion

Effect of calcination conditions

So far, little work has been attempted to determine the calcination conditions of the sol–gel process for NASICON. Thus, the dependence of calcination temperature of the sol–gel method on the properties of NASICON discs was initially investigated. Fig. 2 shows XRD patterns of the NASICON powder samples after calcination at various temperatures. At a heat-treatment temperature >650 °C, a hexagonal NASICON ($Na_3Zr_2Si_2PO_{12}$) phase began to be observed in

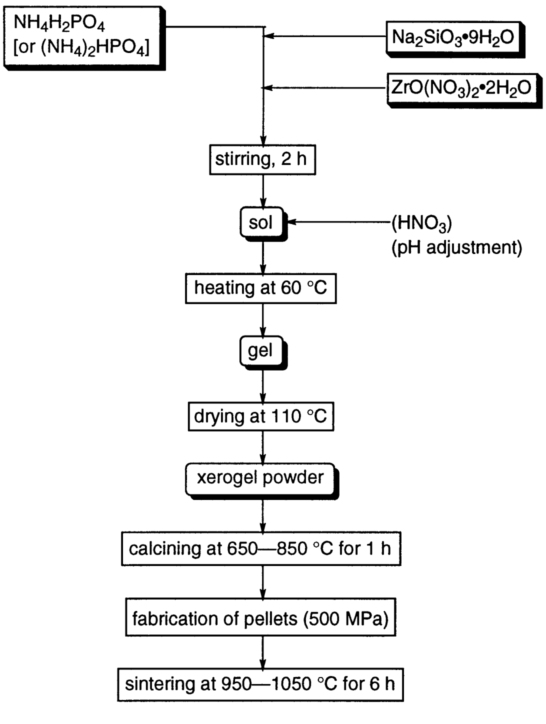

Fig. 1 Preparation process of a NASICON disc by a sol–gel method using aqueous solutions

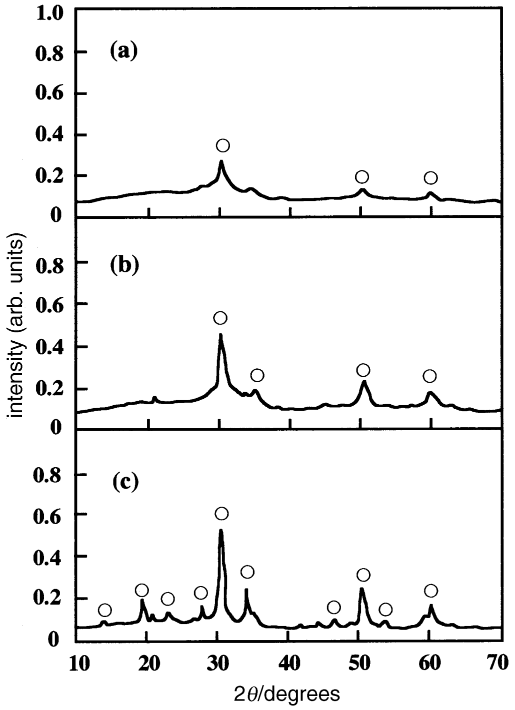

Fig. 2 XRD patterns of NASICON powder prepared by the sol–gel method after calcination at (a) 650 °C, (b) 750 °C, (c) 850 °C (O, $Na_3Zr_2Si_2PO_{12}$)

the XRD patterns of the calcined materials. Well crystallized and almost single-phase NASICON powder was obtained after calcination at 850 °C. In order to establish the optimal calcination temperature, NASICON-sintered discs were prepared from the calcined powder materials. Fig. 3 shows the dependence of calcination temperature on the density and ionic conductivity (at 20 °C) of the NASICON discs after sintering at 1050 °C. The results indicate that the density and ionic conductivity of the NASICON sintered discs, after the heat-treatment at 1050 °C, were largely dependent on the calcination temperature. Both maximum density and ionic conductivity of the NASICON discs were obtained at a calcination temperature of 750 °C. In order to clarify the effect of the calcination conditions, TG–DTA measurements were carried out for the xerogel powder. As shown in Fig. 4, mass losses of the sample were observed with increasing temperature between 100 and 750 °C, and the mass became constant above 750 °C. The endothermic peaks at 150–350 °C and *ca.* 650 °C in the DTA curve are ascribed to the evaporation of decomposed materials and the crystallization of the NASICON phase, respectively.

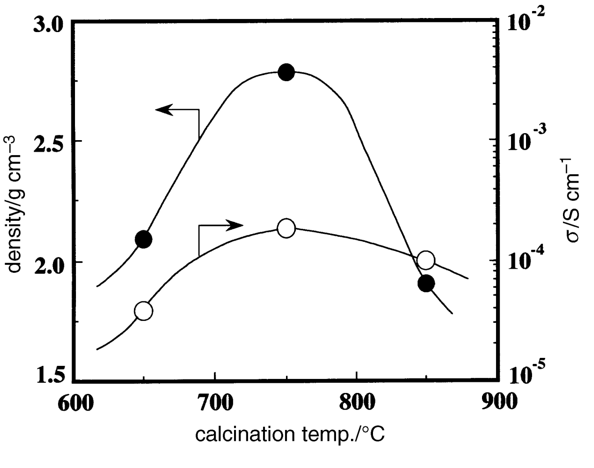

Fig. 3 Effect of calcination temperature on density and ionic conductivity (σ) at 20 °C of NASICON discs after sintering at 1050 °C

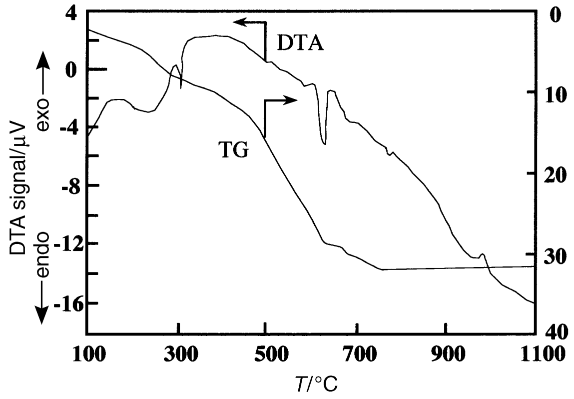

Fig. 4 TG–DTA curves of the xerogel powder

As the mass loss was almost complete at *ca.* 750 °C, the optimal and purest NASICON powder was obtained at this temperature.

Effect of sintering conditions

Fig. 5 shows the dependence of sintering temperature on the properties of the NASICON sintered discs prepared from NASICON powder calcined at 750 °C. Although the density of the sintered discs is scarcely affected by the sintering temperatures, the ionic conductivity of the discs, sintered at either 1000 or 1050 °C, was ten times higher than those sintered at 950 °C, as shown in Fig. 5(a). Although the reason for this result is, as yet, not clear, a slight exothermic peak was observed at *ca.* 980 °C (Fig. 4); a change related to the ionic conduction of Na^+ in the NASICON crystal may occur between 950 and 1000 °C and further investigation is necessary to clarify this mechanism. The effect of the sintering temperature on the formation of a monoclinic zirconia phase, a main secondary phase in NASICON samples, was further investigated. Fig. 5(b) shows the fraction of ZrO_2 in NASICON

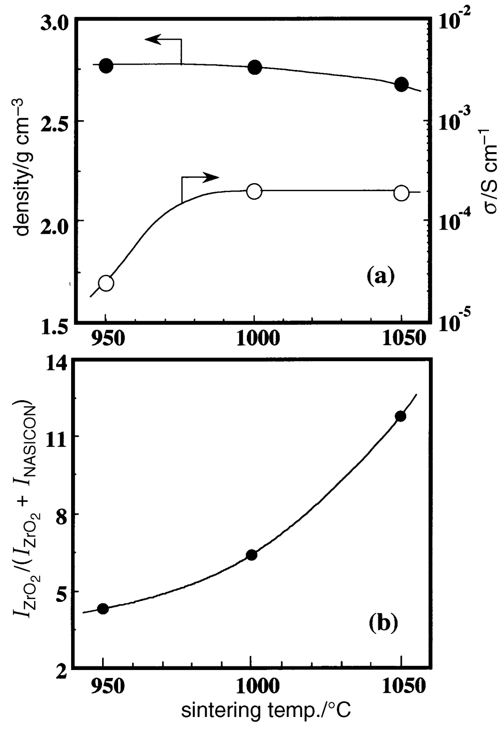

Fig. 5 Effect of sintering temperature on the properties of NASICON discs: (a) density and ionic conductivity (σ) at 20 °C; (b) ratio of ZrO_2 impurity included in the NASICON disc, $I_{ZrO_2}/(I_{ZrO_2}+I_{NASICON})$ (%), compared with the XRD intensity ratio of the $(\bar{1}11)$ line of the ZrO_2 phase (I_{ZrO_2}) to the (116) line of the NASICON phase ($I_{NASICON}$)

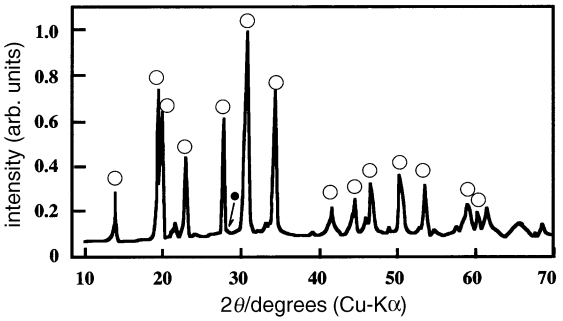

Fig. 6 XRD pattern of a NASICON disc prepared by the sol–gel method (calcination 750 °C, 1 h; sintering 1000 °C, 6 h. O, $Na_3Zr_2Si_2PO_{12}$; •, ZrO_2).

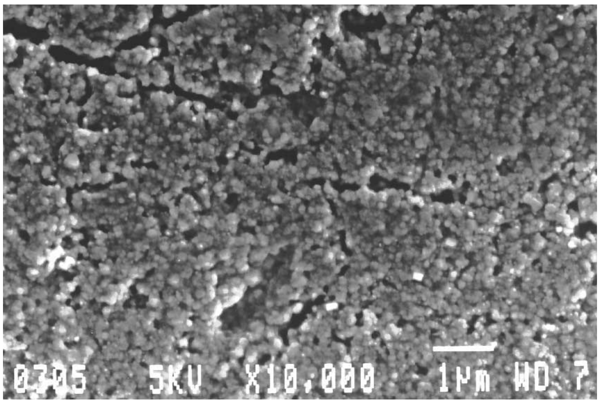

Fig. 7 SEM photograph of a NASICON disc prepared by the sol–gel method (calcination 750 °C, 1 h; sintering 1000 °C, 6 h)

samples as a function of sintering temperature. The fraction of ZrO_2 was defined from the XRD intensity ratio; $I_{ZrO_2}/(I_{ZrO_2}+I_{NASICON})$; where I_{ZrO_2} and $I_{NASICON}$ refer to the ($\bar{1}11$) line of the ZrO_2 phase and the (116) line of the NASICON phase, respectively. The formation of a monoclinic zirconia phase increased almost linearly with increasing sintering temperature. These results led to the conclusion that the best sintering temperature is 1000 °C.

Fig. 6 shows the XRD pattern of a NASICON disc prepared by the optimal heat treatment conditions, *i.e.*, calcination and sintering temperatures of 750 (1 h) and 1000 °C (6 h), respectively. Almost single-phase hexagonal $Na_3Zr_2Si_3PO_{12}$ was obtained from this method and the density of this sample was *ca.* 3.0 g cm^{-3}, corresponding to 92% of the maximum theoretical density. SEM observations revealed that the surface of the NASICON disc was relatively smooth and consisted of homogeneous fine grains of dimensions *ca.* 0.2 µm, as shown in Fig. 7. The ionic conductivity of the disc was high [6.6×10^{-4} S cm^{-1} (at 20 °C)], and almost comparable to the maximum conductivity of samples prepared by previous sol–gel methods.[9,20]

Effect of pH of the sols

All the samples discussed above were prepared from aqueous solutions as mixed, which had a pH = 6.5. It was found that high-density and high-purity NASICON discs were obtained more easily upon controlling the pH of the sol in the first step. The effect of the pH of the sol on the properties of the NASICON discs sintered at 1050 °C is shown in Fig. 8. As shown in Fig. 8(a), the density as well as the ionic conductivity of the NASICON discs were largely dependent on the pH of the sol in the sol–gel method. The best results were obtained for the disc derived from the sol adjusted to pH *ca.* 3.0. It was also observed that the formation of a monoclinic zirconia impurity was minimal at this pH, as shown in Fig. 8(b).

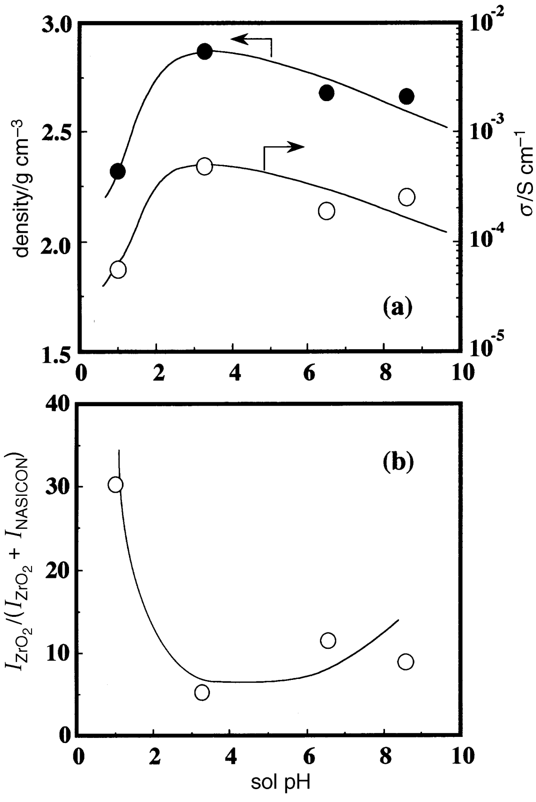

Fig. 8 Effect of pH of the sol on the properties of NASICON discs after sintering at 1050 °C: (a) density and ionic conductivity (σ) at 20 °C; (b) ratio of ZrO_2 impurity included in the NASICON disc, $I_{ZrO_2}/(I_{ZrO_2}+I_{NASICON})$ (%), compared with the XRD intensity ratio of the ($\bar{1}11$) line of the ZrO_2 phase (I_{ZrO_2}) to the (116) line of the NASICON phase ($I_{NASICON}$)

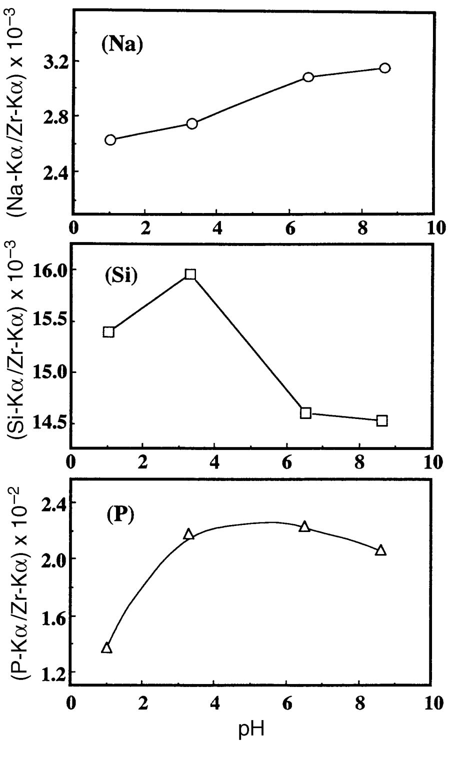

Fig. 9 Effect of sol pH on the relative contents of the elements in NASICON discs

The effect of pH of the sol on the elemental content in the NASICON disc was investigated. Fig. 9 shows the relation between the relative contents of Na, Si and P in NASICON discs with the pH of the sol. The relative content of each element was determined by the intensities of X-ray fluorescence spectra (Na-Kα, Si-Kα and P-Kα), which were normalized to Zr (Zr-Kα). The Na content gradually increased with increasing pH. The P content is almost the same between pH = 3.0 and 9.0, but drastically decreased at pH = 1.0. On the other hand, the Si content was a maximum at pH *ca.* 3. Thus, it seems that Si content plays an important role in the preparation of high-density and high-purity NASICON discs by the sol–gel method, although further investigation is necessary to clarify the synthesis mechanism of NASICON as well as the non-stoichiometry of the preparations.

Conclusions

(1) High-density and relatively high-purity NASICON discs have been prepared by the sol–gel method, using aqueous solutions containing zirconium oxynitrate, ammonium hydrogen phosphate and sodium silicate, using a relatively low processing temperature of 1000 °C.

(2) The properties of the NASICON discs were largely dependent on the calcination and sintering conditions; the optimum temperatures of which were found to be 750 °C (1 h) and 1000 °C (6 h), respectively.

(3) High-density and relatively high-purity NASICON discs were obtained most easily by controlling the pH of the sol in the first step to *ca.* 3.

References

1 Y. Saito, T. Maruyama, Y. Matsumoto and Y. Yano, *Proc. Int. Meet. Chem. Sens., Fukuoka*, 1983, p. 326.
2 S. Yao, Y. Shimizu, N. Miura and N. Yamazoe, *Chem. Lett.*, 1990, 2033.
3 P. Fabry, J. P. Gros, J. F. Million-Brodaz and M. Kleitz, *Sens. Actuators*, 1988, **15**, 33.
4 V. Leonhard, H. Erdmann, M. Ilgenstein, K. Cammann and J. Krause, *Sens. Actuators B*, 1994, **18–19**, 329.
5 T. Takahashi, K. Kuwabara and M. Shibata, *Solid State Ionics*, 1980, **1**, 163.
6 J. B. Goodenough, H. Y-P. Hong and J. A. Kafalas, *Mater. Res. Bull.*, 1976, **11**, 203.
7 H. Y-P. Hong, *Mater. Res. Bull.*, 1976, **11**, 173.
8 R. S. Gordon, G. R. Miller, B. J. Mcentire, E. D. Beck and J. R. Rasmussen, *Solid State Ionics*, 1981, **3/4**, 243.
9 A. Moini and A. Clearfield, *Adv. Ceram. Mater.*, 1987, **2**, 173.
10 Y. L. Huang, A. Caneiro, M. Attari and P. Fabry, *Thin Solid Films*, 1991, **196**, 283.
11 H. Perthuis, G. Velasco and Ph. Colomban, *Jpn. J. Appl. Phys.*, 1984, **23**, 534.
12 H. Perthuis and Ph. Colomban, *Ceram. Inter.*, 1986, **12**, 39.
13 B. E. Yoldas and I. K. Lloyd, *Mater. Res. Bull.*, 1983, **18**, 1171.
14 Ph. Colomban, *Solid State Ionics*, 1986, **21**, 97.
15 Ph. Colomban, *Adv. Ceram.*, 1987, **21**, 139.
16 J-H. Choy, Y-S. Han, Y-H. Kim and K-S. Suh, *Jpn. J. Appl. Phys.*, 1993, **32**, 1154.
17 J. P. Boilot and J. P. Salanié, *Mater. Res. Bull.*, 1979, **14**, 1469.
18 K. D. Kreuer, H. Kohler, U. Warhus and H. Schulz, *Mater. Res. Bull.*, 1986, **21**, 149.
19 D. H. H. Quon, T. A. Wheat and W. Nesbitt, *Mater. Res. Bull.*, 1980, **15**, 1533.
20 A. Clearfield, M. A. Subramanian, W. Wang and P. Jerus, *Solid State Ionics*, 1983, **9/10**, 895.
21 A. Clearfield, P. Jerus and R. N. Cotman, *Solid State Ionics*, 1981, **5**, 30.
22 Y. Shimizu, S. Michishita and T. Murata, *Jpn. J. Appl. Phys.*, 1995, **34**, L833.

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