Spherical particle preparation of Na^+-ion conductive $Na_4Zr_2Si_3O_{12}$ by mist pyrolysis

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Spherical polycrystalline particles of $Na_4Zr_2Si_3O_{12}$ (NZS) have been prepared by a mist pyrolysis technique with alkoxide ethanol solution. Firing the precursor particles, obtained by pyrolysing at 550 °C, yielded the NZS with the highest S/N ratio and the least second phase at ~ 1000 °C. Each spherical particle with an average size of ~ 0.5 μm was composed of primary particles of 0.1 μm diameter after firing. Comparing the particle formation process with the sol–gel, alkoxide pyrolysis and the aqueous solution processes, it would appear that the primary particle size of the mist-pyrolysed NZS depends on the size and residual alkyl group content of the precursor polymers.

1. Introduction

Na^+-ion conductive $Na_4Zr_2Si_3O_{12}$ (NZS), which is one of the end members of NASICON with the general formula $Na_{1+x}Zr_2Si_{3-x}P_xO_{12}$, is a promising material for use as a solid electrolyte because of its stability against molten sodium of the electrode when it is fabricated in solid-state batteries. The total conductivity of polycrystalline ceramics is composed of bulk and grain-boundary conductivity. NZS ceramics have a dominant grain-boundary conductivity because the Na^+-ion sites in the bulk are completely occupied by Na^+ ions and cannot be used for ion hopping. Kohler and Schulz [1, 2] have reported that the conduction barrier of Na^+ ions through the original path in the crystal structure is too high to promote bulk conduction. Therefore the improvement of the grain boundary, which could have many defects convenient for ion migration based on its conduction mechanism, is of primary importance in total conductivity enhancement of ceramic NZS. However, grain-boundary conduction mechanisms have not been strictly defined, such as those of innercrystal bulk regions, because the atomic arrangement and the conduction properties of the grain boundary are sensitive to the extrinsic effects associated with the preparation processes.

The grain-boundary feature of the ceramics primarily depends on the particle size and its surface condition before densification. Grain-boundary conductivity could also change with these particle features which are dominated by preparation processes and starting materials. A mist pyrolysis technique with a solution is a promising process for particle preparation with spherical and uniform particle size which is suitable for the fabrication of high-density ceramics [3]. This process involves the atomization of the solution by an ultrasonic oscillator, and drying and heating of the droplets in a furnace. The droplet size depends on the concentration and viscosity of the starting solution, and the oscillator frequency. Within a droplet, several reactions such as solvent evaporation and atomic rearrangement take place successively to form sintered spherical particles. In the present study, NZS powders were prepared by the mist pyrolysis process. The effects of pyrolysing and subsequent firing temperatures on the degree of NZS formation were examined. The particles obtained by the NZS formation process were also compared with the NZS particles from other preparation techniques.

2. Experimental procedure

The mist pyrolysis apparatus is shown in Fig. 1. The mist of the solution, generated by an ultrasonic oscillator with a frequency of 1 MHz, flowed through the furnace, which preserved the temperature gradient, with nitrogen carrier gas at $1.0 \, l \, min^{-1}$. The temperature in the lowest part (T_3), of the furnace, was controlled in the range of 500–800 °C. The retention time of the mist in the furnace was about 30 s. The pyrolysed precursor powder was collected by the glass filter (G3) positioned at the end of the furnace. The powder was refired at 800–1300 °C to form the crystalline powder.

An aqueous solution of the starting solution was prepared by mixing the $Si(OC_2H_5)_4$ ethanol solution and aqueous solutions of $NaNO_3$ and $ZrO(NO_3)_2 2H_2O$ and stirring for 1 h. An alkoxide ethanol solution of another starting solution was prepared using CH_3ONa, $Zr(OC_4H_9)_4$, $Si(OC_2H_5)_4$. The mixture of these alkoxide ethanol solutions was refluxed with stirring for 12 h until the viscosity in-
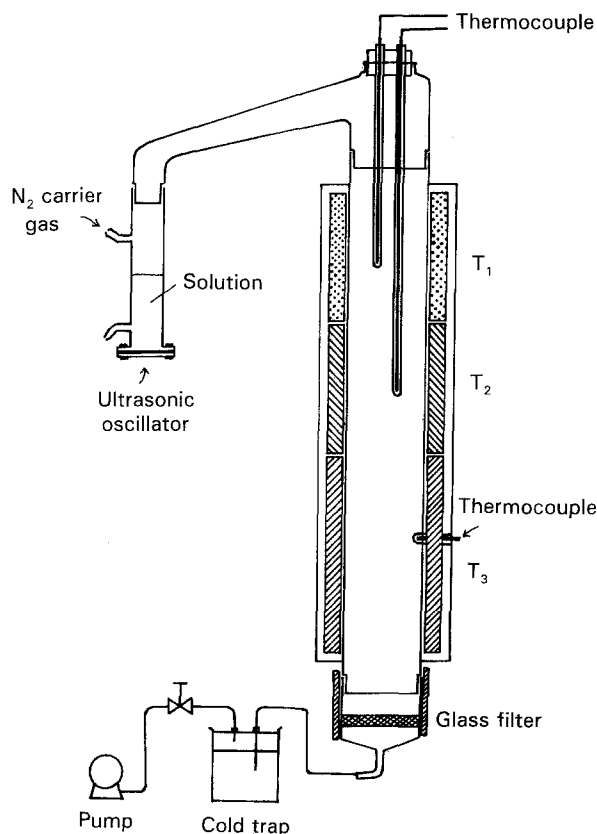
Figure 1 The mist pyrolysis apparatus. The frequency of the ultrasonic oscillator is 1 MHz. The furnace is composed of three parts, T_1 and T_2 each 30 cm long, and T_3 50 cm long, and the temperature is controlled in each.

creased compared with the initial solution and the colour changed to yellow.

Powders of these solutions were dried at 120 °C in an oven, and then fired at 800–1200 °C to obtain NZS particles without using mist pyrolysis process. In this case (the sol–gel process without mist pyrolysis), the alkoxide ethanol solution was refluxed for 5 h and further refluxed for 12 h after hydrolysation with excess water for gelation. The precursor gel was dried at 120 °C and then fired at 800–1300 °C to achieve crystallization. The flow charts of these preparation processes are illustrated in Fig. 2.

The carbon contents of the precursor particles were analysed from the i.r. absorption intensity after pyrolysis in an oxygen atmosphere.

All compounds were identified from the X-ray diffraction (XRD) patterns. Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were performed using the Rigaku Denki, TAS 200. The size and microstructural features of the particles were observed using the free emission scanning electron microscopy (FE-SEM S-5000, Hitachi Ltd).
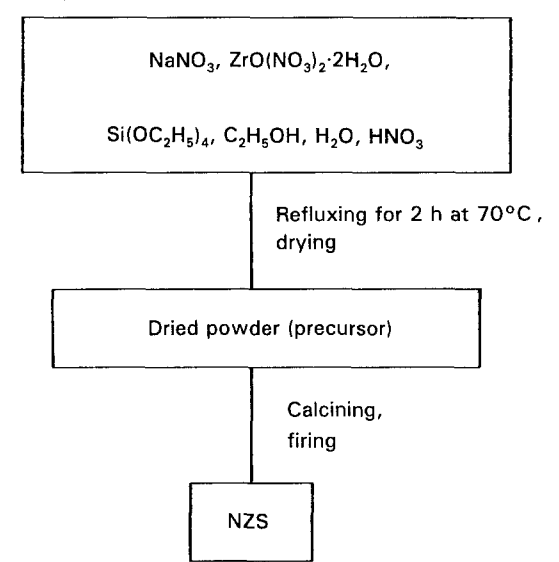
3. Results and discussion

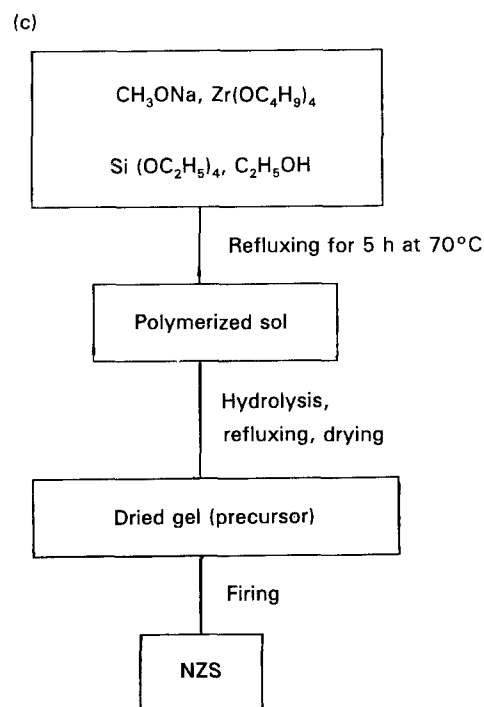### 3.1. NZS preparation by the mist pyrolysis process

The mist pyrolysed powder, using the aqueous solution, exhibited SiO_2 and ZrO_2 components without NZS in the XRD patterns after firing. Furthermore, the middle part of the quartz tube in the furnaces was
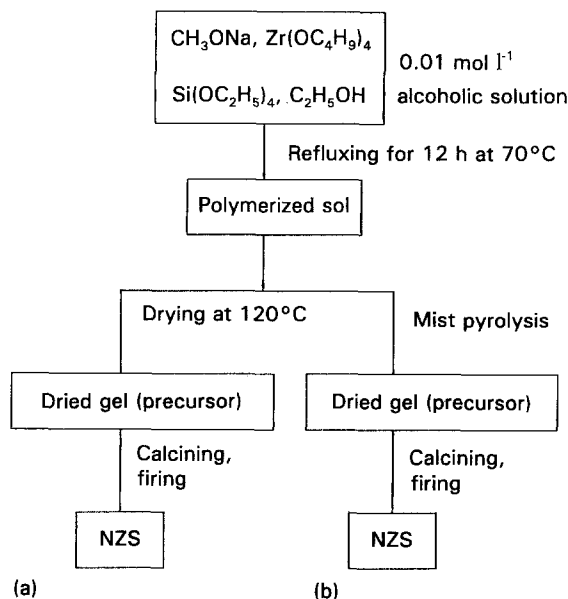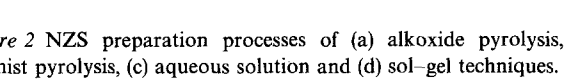

Figure 2 NZS preparation processes of (a) alkoxide pyrolysis, (b) mist pyrolysis, (c) aqueous solution and (d) sol–gel techniques.

eroded. Thus, it was presumed that the quartz reacted with basic sodium and, consequently, residual components of the solution were eliminated. This result suggests that the aqueous solution in which each initial component would scarcely form the network structure is not suitable for NZS preparation by mist pyrolysis.

The use of a refluxed alkoxide ethanol solution in the mist pyrolysis process resulted in precursor particles of NZS in the pyrolysing temperature range 500–800 °C. The refluxing time of the solution was significant for the formation of high-purity NZS particles, because the XRD peak intensity of the second phase, $Na_2ZrSi_2O_7$, increased with decreasing refluxing time. The starting solution showed some degree of polymerization after refluxing for 12 h, because it became viscous and yellow. Therefore, the polymerized precursor structure would be convenient for preserving the chemical composition of NZS even after atomization. Pyrolysing the mist particles of the alkoxide solution in the temperature range 550–800 °C produced a black precursor powder of NZS, although pyrolysing at 500 °C resulted in a light-brown powder. The black powder may contain intermediate carbides as a result of the imperfect combustion of alkoxide compounds in a nitrogen atmosphere above 550 °C.

Fig. 3 shows the DTA and TG results of the precursor powder obtained by mist pyrolysis and direct alkoxide pyrolysis for comparison. Both DTA curves showed two main exothermic peaks at 300–500 °C and ~800 °C, both of which were accompanied by a weight loss. The first exothermic process at 300–500 °C should be identified as the oxidation reaction of the residual alcohol of the solvent or that produced by hydrolysis [4]. The starting temperature and the strength of the peak depended on the sample.
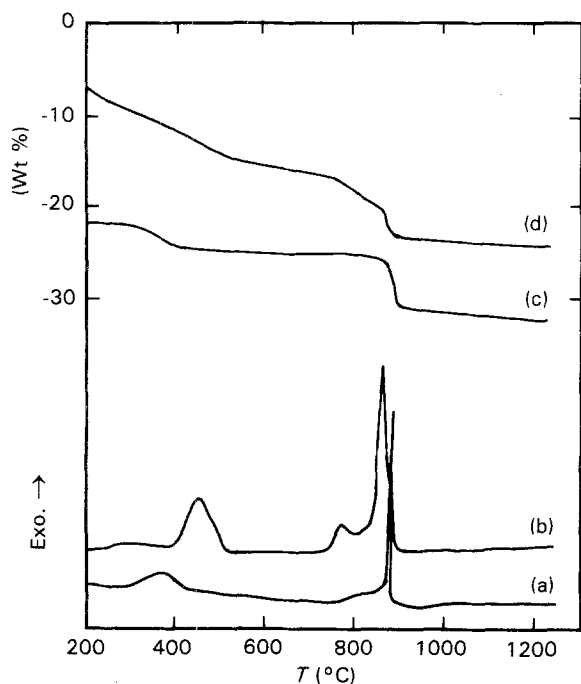
The other peak in the vicinity of 800 °C could be assigned to the combustion of residual alkyl groups on the precursor powder, because the weight loss in TG was almost consistent with the carbon content analysed by i.r. absorption of CO_2 after combustion of the precursor powder in an oxygen atmosphere. As the larger carbon content was observed in the precursor combusted at 900 °C compared with that combusted at 700 °C (15 times), it could be said that the residual carbide would almost be desorbed at 800 °C. Furthermore, it appears that the NZS changes from amorphous to crystalline at ~800 °C, from the XRD results. Therefore, the two processes, carbon combustion and crystallization, would occur competitively at ~800 °C. It is also shown that the DTA peak at 800 °C of the mist pyrolysis precursor is also sharper and the weight decrease is more stepwise compared with those of the alkoxide pyrolysis. This suggests that the precursor particles obtained by mist pyrolysis are homogeneous in chemical composition, because each droplet with uniform particle size was heated while passing through the quartz tube under the same conditions. It appears that mist pyrolysis is profitable for the preparation of homogeneous particles, even in complicated ternary phases such as NZS.

The S/N ratio of NZS and second-phase intensity of the XRD peaks pyrolysed at several temperatures are

Figure 3 DTA and TG curves of precursor powders of (a, c) mist pyrolysis and (b, d) alkoxide pyrolysis, respectively. Heating rate $= 10 °C\,min^{-1}$.
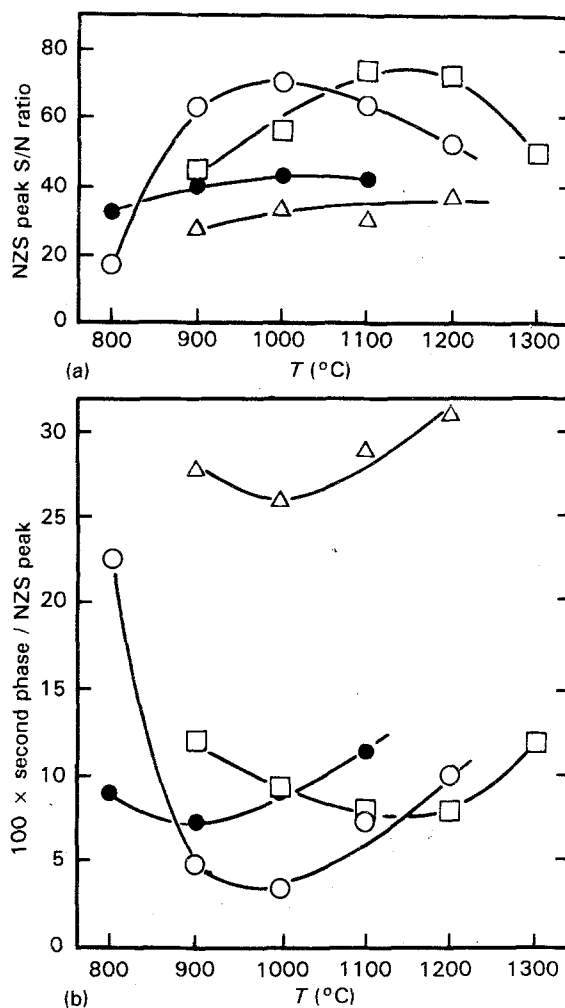

Figure 4 (a) NZS S/N ratios and (b) second-phase intensity of the XRD peaks by mist pyrolysis at (●) 500 °C, (○) 550 °C, (□) 700 °C, (△) 800 °C as a function of firing temperature.

plotted in Fig. 4 as a function of final firing temperature of the precursor powder. Pyrolysing at 550 and 700 °C gave the highest S/N ratios which were comparable to those of NZS obtained from the direct alkoxide pyrolysis. On the other hand, pyrolysing at 800 °C produced the NZS with a low S/N ratio and a high second-phase content. This result suggests that the mono-valent Na^+ ions coordinated at the end of the polymer network tend to be eliminated in the mist pyrolysing process. Furthermore, this result shows that the precursor pyrolysed at lower temperatures had a maximum S/N ratio and a minimum second-phase intensity at lower firing temperature. The lowest firing temperature for crystallization was 800 °C for the amorphous precursor obtained by mist pyrolysis at 550–600 °C. On the other hand, the precursor pyrolysed at 700 and 800 °C, which was still amorphous, did not crystallize, even on firing at 800 °C. This suggests that mist pyrolysis at temperatures higher than 700 °C would promote the elimination of Na^+ ions and an inhomogeneous atomic arrangement in the amorphous powder.

The eliminated phases, except for NZS, were assigned to $Na_2ZrSi_2O_7$ and ZrO_2, and were observed at all pyrolysing and firing temperatures. These phases also suggest the tendency of the Na^+ component to be eliminated because the following process could be expected from this observation

$$Na_4Zr_2Si_3O_{12} \rightarrow Na_2ZrSi_2O_7 + ZrO_2$$
$$+ SiO_2 + Na_2O \qquad (1)$$
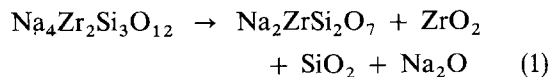
On the other hand, Na_2ZrSiO_5 was eliminated only in the alkoxide pyrolysis process, and decreased with increasing firing temperature, although they had the same starting materials [5]. Therefore, it is expected that the precursor structure in the mist pyrolysis differs in atomic arrangement from that of the alkoxide pyrolysis, due to the difference in the heat conduction rate between a droplet of the mist and the conventional powder.

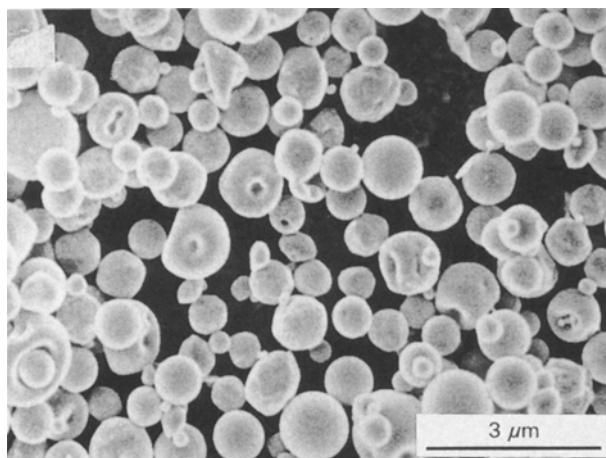Fig. 5 shows scanning electron micrographs of the mist pyrolysis particles. The precursor powder containing residual carbides consisted of spherical particles, some of which were dimpled at the particle centre. Even after firing at 800 °C, particles larger than 0.5 μm diameter remained spherical, but the surface was not smooth and showed a tendency of division in to primary particles. It appears that mist pyrolysis is suitable for the preparation of spherical uniform-sized particles.

It should be considered that grain-boundary conductivity depends not only on the secondary particle condition but on the primary particle size and their tendency towards aggregation . This is because the finally sintered ceramics were composed of an aggregation of primary particles. In the mist pyrolysis process, it appeared that the polymerization process of the starting solution was significant in the preparation of pure NZS, indicating that the uniformly polymerized precursor structure is profitable for the minimization of component elimination and the smooth rearrangement into NZS crystal structure. Therefore, the precursor structure contributes to the properties of the product, such as the S/N ratio and the included second-phase content, which would reflect the formation degree in the process. Therefore, the mechanism by which the polymerized amorphous structure rearranges to the crystalline form, should be considered in relation to the dominant factors such as polymerization degree and residual alkyl group content. For this purpose, three different processes, the sol–gel process with alkoxides, the alkoxide pyrolysis process, and the aqueous solution process, were investigated.

3.2. NZS preparation by the sol–gel, alkoxide pyrolysis and aqueous solution processes, and consideration of their formation processes

NZS preparation by the sol–gel process had poor reproducibility compared with the alkoxide pyrolysis and the aqueous solution processes. It was presumed that the polymerized precursor composed of three alkoxides tended to be inhomogeneous after hydrolysis, because the hydrolysis rates of each of the alkoxides were different.

Scanning electron micrographs of sintered NZS pellets from three processes are shown in Fig. 6. The average primary particle sizes roughly estimated from the photographs were ~1, 0.1 and 0.3 μm for NZS from aqueous solution, alkoxide pyrolysis and sol–gel, respectively. The size of the alkoxide-pyrolysed NZS was almost the same as that of the primary particles of mist-pyrolysed NZS. If a precursor polymer size after hydrolysis is assumed to be a few tens of nanometres in diameter, which was generally accepted in silica gel preparation from alkoxide [6], a sol–gel NZS particle could be estimated to be composed of about ten polymers. On the other hand, the polymer size of alkoxide-pyrolysed NZS would be smaller, because there is no hydrolysis reaction in this process to promote the polymerization. Comparing the particle sizes of alkoxide-pyrolysed NZS and sol–gel NZS from the scanning electron micrographs, the precursor polymer size obtained by alkoxide pyrolysis would roughly be estimated to be about 5–10 nm.
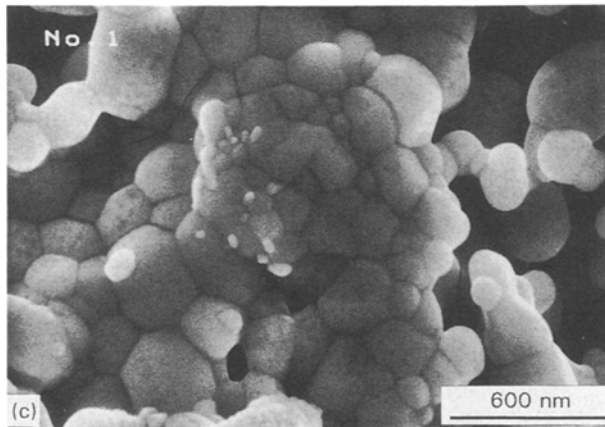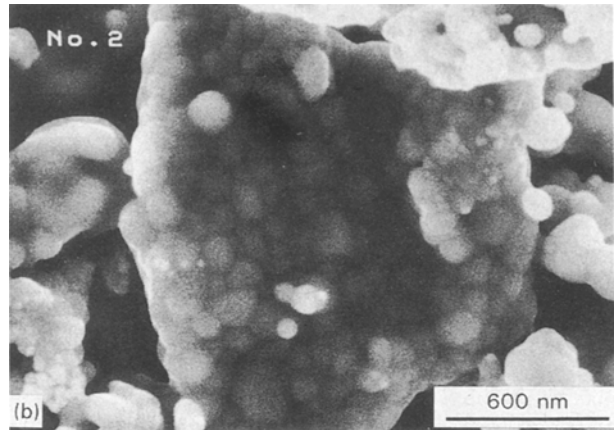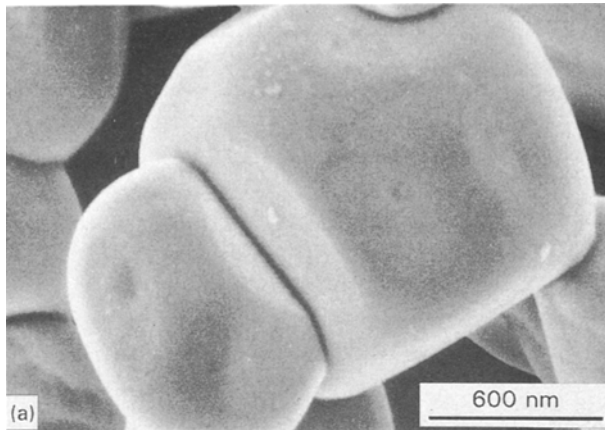

Figure 5 Scanning electron micrograph of the mist pyrolysis precursor particles.

Figure 6 Scanning electron micrograph of NZS ceramics prepared by (a) aqueous solution, (b) alkoxide pyrolysis and (c) sol–gel processes.

tion assume the role of active and initial sites for subsequent crystal and particle growth [5].

4. Conclusion

NZS spherical particles were obtained by a mist pyrolysis technique with an alkoxide ethanol solution. The spherical particles were composed of an aggregation of fine primary particles after firing of the precursor particles. From a comparison of alkoxide ethanol and aqueous solutions, it appears that the polymerized solution was suitable for the preparation of uniform NZS ceramics because the homogeneous chemical component could be preserved within each mist droplet even in the pyrolysis process. Furthermore, the polymer size and the residual content of alkyl groups of the precursor particles were responsible for the primary particle size of the final product when the alkoxide alcohol solution was used as the starting material.

References

1. H. KOHLER and H. SCHULZ, *Mater. Res. Bull.* **20** (1985) 1461.
2. *Idem, ibid.* **21** (1986) 23.
3. H. KAMIYA, H. SUZUKI, D. KATO and G. JIMBO, *J. Am. Ceram. Soc.* **76** (1993) 54.
4. S. SAKKA, "Science of the sol–gel process" (Agunesyofusya, Tokyo, 1988).
5. Y. SAITO, Y. YAMAMOTO and O. NAKAMURA, *Solid State Ionics*, submitted.
6. G. ORCEL and L. L. HENCH, *Ceram. Eng. Sci. Proc.* **5** (718) (1984) 546.

Therefore, it could be said that the particle-size difference between the sol–gel NZS and alkoxide-pyrolysed NZS, in spite of the same starting materials, primarily comes from the difference in the precursor polymer size. The hydrolysis reaction which initially promotes the polymer growth occurred little in alkoxide pyrolysis because of the lack of water. Therefore, each polymer of the alkoxide pyrolysis did not grow into a large network, compared with that of the sol–gel process. As a result, the precursor of the alkoxide pyrolysis had a relatively larger amount of residual alkyl groups compared with the sol–gel precursor. The alkyl groups which had not been eliminated in the precursor formation process would influence particle growth because they are finally combusted in the firing process at $\sim 800\,^\circ$C, as confirmed by DTA results. Furthermore, the atomic configuration of the amorphous NZS precursor rearranges to the crystalline form at $\sim 800\,^\circ$C. The competitive reactions of alkyl-group elimination and atomic rearrangement at $800\,^\circ$C, therefore suggest that the residual alkyl groups dominate the primary particle size of NZS because it is probable that the sites of the alkyl group after elimina-