Synthesis and properties of nasicon prepared from different zirconia-based precursors

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This work reports on the synthesis and characterization of NASICON prepared from SiO_2 , $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and two types of zirconia: pure monoclinic ZrO_2 and TZP (Tetragonal Polycrystalline Zirconia, with 3 mol% Y_2O_3) as raw materials. The classical ceramic method was used in all cases. SEM, XRD and DTA were used to follow the synthesis and sintering process, and impedance spectroscopy (IS) was used to study the electrical properties of sintered pellets. Results obtained with different NASICON samples showed a significant role of composition and processing conditions on the electrical properties. Samples based on TZP, sintered at 1210°C , exhibited densities of about 3.20 g/cm^3 (98% of theoretical density of NASICON) and ionic conductivities of about $2 \times 10^{-3} \text{ S.cm}^{-1}$ at room temperature a rather interesting result when compared with data obtained with the material prepared from pure ZrO_2 .

Keywords: NASICON; solid electrolyte; impedance spectroscopy; sodium ionic conductors, synthesis

Síntesis y propiedades de Nasicon preparado a partir de diferentes precursores basados en circonia

Este trabajo trata de la síntesis y caracterización de NASICON preparado a partir de SiO_2 , $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ y dos tipos de circonia, ZrO_2 monoclinica pura y TZP (circonia policristalina tetragonal, con 3 moles% Y_2O_3) como materia prima. Se emplea el método cerámico clásico en todos los casos. Las técnicas de MEB, DRX y ATD se emplean para seguir la síntesis y el proceso de sinterización. La espectroscopia de impedancia compleja se emplea para estudiar las propiedades eléctricas de las muestras sinterizadas. Los resultados obtenidos con diferentes muestras de NASICON mostraron un papel significativo de la composición y condiciones de procesamiento sobre las propiedades eléctricas. Las muestras basadas en TZP, sinterizadas a 1210°C , presentan densidades alrededor de 3.20 g/cm^3 (98% de la densidad teórica del NASICON) y conductividad iónica de $2 \times 10^{-3} \text{ S.cm}^{-1}$ a temperatura ambiente, un resultado bastante interesante cuando se compara con datos obtenidos con material preparado de ZrO_2 pura.

Palabras clave: Electrolito sólido, espectroscopia de impedancia, conductores iónicos de sodio, síntesis

1- INTRODUCTION

NASICON is a well known family of sodium ionic ceramic conductors, with a large range of allowed stoichiometries $\text{Na}_{1+x}\text{Zr}_x\text{Si}_{3-x}\text{P}_3\text{O}_{12}$ with $0 < x < 3$ (1,2). The highest ionic conductivity is obtained for $x = 2$, corresponding to a monoclinic structure (3). This family of materials is attracting a large attention because of a high ionic conductivity and claimed stability in humid air and aqueous solutions (4). NASICON-type ceramics have a low stability in contact with molten sodium or molten sodium salts (5).

NASICON can be synthesized by two major methods: a ceramic route and a sol-gel route. The first method is based on mechanical mixing of the raw compounds, usually by ball-milling. After calcination of all precursors at intermediate temperatures, the powders are pressed and fired again to obtain dense specimens. Due to the requirement of a higher sintering temperature (close to the melting temperature), a monoclinic ZrO_2 phase is always present as a second phase in samples prepared by this method (6). The alternative sol-gel route has been the most successful technique to get very fine powders and is based on hydrolysis-polycondensation reactions of alkoxides in alcohol medium, with an excess of water and under strong stirring (7,8). Following this route, low sintering temperatures can be used and Na and P losses can be avoided (9). At present,

NASICON solid electrolyte thin or thick films are used for ISE (ion selective electrodes) or gas sensor devices (10,11).

The synthesis and electrical properties of NASICON-type compounds obtained by mechanical mixing of raw materials were studied in this work. The TZP (Tetragonal Polycrystalline Zirconia) powder used in this study with 3 mol% Y_2O_3 shows a high reactivity due to a very small particle size (submicrometer). The main expected advantage of this alternative solution was a favorable reaction kinetics at low temperature. Previous studies on yttrium-doped NASICON used Y_2O_3 as a direct precursor (12) or to replace SiO_2 (13,14). However, in all cases monoclinic ZrO_2 was used as a starting material.

2- EXPERIMENTAL

2-1 Preparation of the samples

Two kinds of NASICON compounds were prepared: the classical $\text{Na}_3\text{Si}_2\text{Zr}_2\text{PO}_{12}$, starting from pure monoclinic ZrO_2 , and a derived material starting from TZP as a precursor, hereby called NASICON-TZP with a nominal formula $\text{Na}_3\text{Zr}_{1.94}\text{Y}_{0.06}\text{Si}_2\text{PO}_{12}$. No excess of Na was added to compensate for the charge unba-

TABLE 1. SUMMARY OF DATA ON NASICON-TYPE MATERIALS.

Sample	Sintering Temperature (°C)	Density (g/cm ³)	Conductivity 25°C (S cm ⁻¹)
NASICON-TZP (*)	1230 (10 h)	3.25	9x10 ⁻⁴
NASICON-TZP (*)	1210 (10 h)	3.20	2.15x10 ⁻³
NASICON-TZP (*)	1190 (10 h)	3.17	1.4x10 ⁻³
NASICON (15)	1280 (8 h)	3.15	4.4x10 ⁻⁴
NASICON Sol Gel (5)	1100 - 1200	3.05 - 3.18	1x10 ⁻³
NASICON (2%mol Y)(12)	1200 (10 h)	—	7x10 ⁻⁴ (**)
NASICON (5%mol Y)(12)	1200 (10 h)	—	2x10 ⁻³ (**)

(*) this work.

(**) estimated value

lance due to the replacement of Y³⁺ for Zr⁴⁺. This leaves open the identification of the type of defects created to compensate for this substitution. Besides pure ZrO₂, TZP (from TOSOH), Na₃PO₄·12H₂O and SiO₂ were used as raw materials.

All starting materials were mixed in a ball mill with ethanol, dried in a stove (60°C) and calcined in air at several temperatures. The calcined powders were wet-milled again for 2 h. Pellets of 1 cm diameter and a few mm thick were uniaxially pressed (98 MPa). No binder was used. Sintering took place at temperatures between 1180°C and 1230°C, in air, for 10 h. Pellets were placed in a Pt crucible and covered during sintering to avoid major losses due to volatilization. Following this procedure, good specimens were obtained for NASICON-TZP but only poor densities could be obtained for classical NASICON. An alternative solution was thus adopted to prepare the latter composition, following a route previous developed and reported (15). The pre-calcined material was pressed and fired under vacuum at 900°C, for 2 h, before final sintering in air at 1280°C for 16 h. The intermediate step under vacuum is used to eliminate organic binders introduced before pressing. Attempts to remove these binders in air, at atmospheric pressure, failed due to formation of defects related to the decomposition of the binder.

2-2 Characterization of samples

Thermal analysis (DTA, TGA) of mixed powders and calcined powders were performed up to 1100°C. Powders calcined at different temperatures and sintered samples were characterized by X-Ray Diffraction (XRD) using CuKα radiation. The microstructural characterization was based on observation of samples by Scanning Electron Microscopy (SEM), after polishing and thermal etching at 1100°C.

Polished pellets were coated with Pt paste for electrical measurements. To eliminate the organic solvent and binder, and to sinter the Pt electrode to the ceramic, samples were heated at 700°C for 30 min. A Hewlett Packard 4284A LCR meter was used to perform Impedance Spectroscopy (IS) measurements between 0°C and 200°C, in the frequency range from 20 Hz to 1 MHz.

3- RESULTS AND DISCUSSION

3-1 Structural and microstructural features

Figure 1 shows the X-ray diffraction patterns of NASICON and NASICON-TZP calcined at different temperatures.

Diffraction peaks of unreacted ZrO₂ and TZP can be seen in powders calcined at 900°C during 8 h. At such a low temperature, there is no evidence of NASICON formation when a pure monoclinic zirconia is used as a precursor, but the formation of NASICON is clearly seen when using TZP as a precursor. The pattern of similar powders calcined at 1100°C during 8 h already exhibit every characteristic diffraction line of NASICON. As a summary, diffraction peaks corresponding to a small amount of monoclinic ZrO₂ are presented in the case of NASICON while none of them is observed in the course of formation of NASICON-TZP. Also formation of NASICON-type compounds occurs at earlier stages when TZP is used as a precursor. All these remarks suggest that the high reactivity of the TZP powders was indeed an important parameter in the entire synthesis route.

X-ray diffraction patterns of sintered samples of NASICON and NASICON-TZP are shown in Figure 2. Both of them exhibit diffraction lines typical of monoclinic ZrO₂. In the NASICON-TZP pattern the relative intensity of these lines suggests that the amount of monoclinic ZrO₂ is smaller than that for NASICON, although the sintering temperatures are slightly lower in the former case.

The formation of monoclinic ZrO₂ as a second phase during NASICON-TZP synthesis requires loss of yttrium from TZP during the high temperature treatment. As NASICON main

Figure 1- XRD of calcined NASICON and NASICON TZP powders, at different temperatures. At 1100°C, the strongest lines of monoclinic ZrO₂ are not present.

peaks develop well before the formation of monoclinic zirconia (Figure 1), the entire process must involve more than one stage. One first step might be partial consumption of TZP due to reaction with the remaining precursors, with formation of NASICON-TZP. The subsequent formation of monoclinic zirconia might be the result of either loss of yttrium from the unreacted TZP to the NASICON phase, or due to precipitation of ZrO_2 from the NASICON-type phase, following Na and P losses during the high temperature sintering.

Figure 3 shows SEM micrographs of NASICON and NASICON-TZP sintered samples after polishing and thermal etching. NASICON exhibits heterogeneous grain size between $1\text{ }\mu\text{m}$ and $6\text{ }\mu\text{m}$, and the presence of liquid phase between grains is suggested in some observations. This is a direct consequence of the high sintering temperatures employed to get well densified pellets, close to the melting temperature.

An homogeneous grain size of about $1\text{ }\mu\text{m}$ is evidenced in the case of NASICON-TZP pellets. No vestige for the formation of a liquid phase could be noticed in this case. Simple observation of the microstructures previously presented also suggests that the densification of NASICON-TZP is higher than found for the classical NASICON composition. Sintering to almost full densification at lower temperatures was indeed one expected advantage for the use of the reactive TZP powder.

A comparative table (Table 1) shows the main differences and similarities between NASICON samples obtained in this work and in previous publications. A relatively high density is found for NASICON-TZP, which is 98 % of theoretical density of the classical NASICON (3.27 g/cm^3). This result, clearly contradicted by the observed microstructures suggesting a porosity of a few %, neglects the partial replacement of Y for Zr and possible charge compensation mechanism. This means that, in fact, the theoretical density of NASICON-TZP should be higher than that found for the classical composition.

Zr is slightly heavier than Y. If an almost constant unit cell volume is assumed for materials lightly doped with Y, a lower density must be expected with respect to the classical composition. Compensation for the negative defects formed with the introduction of Y in the lattice (presumably Y_{Zr}' , if the Kröger-Vink type notation is adopted), can only be achieved by formation of interstitial metals or oxygen vacancies. The former would be coherent with increased theoretical density, while the latter should result in a lower density. Work is in progress to try to elucidate this issue.

3-2 Electrical Properties

Figure 4 shows the typical impedance spectra at 0°C of NASICON and NASICON-TZP samples sintered at different temperatures. Due to the considerably higher impedance of the NASICON pellet, the corresponding spectrum is shown in a separate diagram. Low temperature measurements were found essential to try to distinguish the bulk from the grain boundary contribution. Even at 0°C , only the grain boundary arc is clearly seen and the bulk contribution can only be estimated from the high frequency intercept of the grain boundary arc. Simple inspection of the spectra shown in Figure 4-a suggests that the major differences between these materials are mostly due to the grain boundary contribution as all high frequency intercepts of the grain boundary arcs are close to each other. This is not the case for the NASICON pellet. Both the bulk and grain boundary contributions tend to be higher.

Figure 2- XRD of sintered NASICON and NASICON TZP pellets. Dashed lines show the positions of the main monoclinic ZrO_2 diffraction peaks.

Figure 3 - SEM micrographs of NASICON (a, b) and NASICON TZP (c, d) sintered samples, with different magnifications.

At room temperature, NASICON shows a total ionic conductivity of about $4 \times 10^{-4}\text{ Scm}^{-1}$, while for NASICON-TZP sintered at 1210°C , this conductivity is $2.1 \times 10^{-3}\text{ Scm}^{-1}$.

The activation energy for total ionic conduction was estimated from Arrhenius plots of $\log(\sigma \cdot T)$ against $1/T$, shown in figure 5. In a range of temperatures between 0°C and 180°C , the activation energies calculated for NASICON and NASICON-TZP (sintered at 1230°C) were 0.39 eV and 0.36 eV respectively. NASICON-TZP samples sintered at lower temperatures showed activation energies of about 0.31 - 0.32 eV. This difference is probably due to the grain boundary contribution, clearly dominating the electrical performance of samples fired at high temperatures. In particular, in case of the NASICON sample, a liquid phase could be clearly identified along the grain boundaries, which is known to justify a low temperature ion-blocking behavior. On the contrary, for NASICON-TZP pellets fired at lower temperatures, the relatively small grain boundary contribution vanishes even at low temperature, and

Figure 4 - Nyquist plots at 0°C of a) NASICON-TZP and b) NASICON samples sintered at different temperatures.

Figure 5 - Arrhenius-type plots of total conductivity (s) as a function of absolute temperature (T). Activation energies estimated from these plots were 0.39 eV for NASICON sintered at 1280°C (u), 0.36 eV for NASICON-TZP sintered at 1230°C (D), 0.32 eV for NASICON-TZP sintered at 1190°C (o) and 0.31 eV for NASICON-TZP sintered at 1210°C (°).

the bulk contribution tends to control the entire electrical performance. This explains the close vicinity between data obtained for the two samples fired at lower temperatures. This also means that these lower values of the activation energy should be closer to the actual migration enthalpy of sodium ions in this structure, rather than to those obtained with the remaining pellets.

4- CONCLUSIONS

Due to the use of a high reactivity powder (TZP), NASICON-type materials could be processed and sintered at lower temperatures than required for the classical ceramic route using a conventional ZrO_2 powder. The major consequences of this alternative procedure were the production of dense pellets with smaller content of monoclinic zirconia, homogeneous microstructures without any vestiges of liquid phase, overall high electrical conductivities, and a significant benefit in the abatement of the grain boundary impedance. While the exact charge compensation mechanism associated with the partial replacement of Y^{3+} for Zr^{4+} is still unknown, materials characteristics with influence on potential applications were improved with this procedure.

ACKNOWLEDGMENTS

Financial support from the Alfa Program (CEC, Brussels) is greatly appreciated. The authors express their thanks to Dr. Filipe Figueiredo for his helpful collaboration.

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