Restrictions to obtain NASICON by a ceramic route

R.O. FUENTES[1], D.G. LAMAS[1], M.E. FERNANDEZ DE RAPP[1], F.M. FIGUEIREDO[2,3], J.R. FRADE[2], F.M.B. MARQUES[2], J.I. FRANCO[1]

[1] CINSO-CITEFA-CONICET, J.B de La Salle 4397, B1603ALO Villa Martelli, Buenos Aires, Argentina.
[2] Ceramic and Glass Engineering Department, CICECO, University of Aveiro 3810-193 Aveiro, Portugal
[3] Science and Technology Dep., Universidade Aberta, R. da Escola Politécnica 147, 1269-001 Lisbon, Portugal

Highly reactive monoclinic ZrO_2 powders were mixed with $Na_3PO_4 \bullet 12H_2O$ and amorphous SiO_2 in the stoichiometric quantities to obtain $Na_3Zr_2Si_2PO_{12}$. The mixtures were calcined at different temperatures (T_{calc}) and for variable periods of time (t_{calc}). Their morphology was analysed by SEM and the composition by powder XRD. NASICON reflections are not detected for T_{calc}=900°C and for relatively short t_{calc} values of 2 h. At 1100°C, the onset of low intensity NASICON peaks indicate the early stages of the formation reaction which is significantly enhanced when T_{calc} increases up to 1200 and 1300°C. For higher temperatures, an apparent decrease of the reaction rate is suggested. On the other hand, the intensities of the ZrO_2 peaks suffer a drastic decrease when T_{calc} varies from 900 to 1300°C, followed by a slight increase for T_{calc}=1400°C. The studies were extended for mixtures kept in isothermal conditions at 1100, 1200 and 1300°C during 0.5, 1, 2, 4, 8 and 16 h. In the three temperatures, the increase of the t_{calc} up to ca. 4 h leads to a significant increase in the intensity of the NASICON reflections while that of $mZrO_2$ decreases. A plateau is apparent for higher t_{calc} values suggesting that equilibrium may be attained. The use of a highly reactive tetragonal zirconia powder (also thermodynamically unstable at low temperature) clearly improved the overall reaction extension and kinetics at moderate temperatures, yielding a single phase product.

Keywords: NASICON, microstructure, solid state reaction, XRD.

Restricciones para obtener nasicon por una ruta cerámica

Polvos de ZrO_2 monoclínica altamente reactivos fueron mezclados con $Na_3PO_4 \bullet 12H_2O$ y SiO_2 amorfo en cantidades apropiadas para obtener $Na_3Zr_2Si_2PO_{12}$. Las mezclas fueron calcinadas a diferentes temperaturas (T_{calc}) y diferentes tiempos (t_{calc}) y caracterizadas por SEM y DRX. Líneas características del NASICON no son detectadas a T_{calc}=900°C y a tiempos de calcinado relativamente cortos (< 2h). A 1100°C, la presencia de picos de NASICON de baja intensidad indica los primeros momentos de la reacción de formación, la cual es significativamente mejorada cuando T_{calc} es aumentada a 1200 y 1300°C. Para altas temperaturas (<1300ºC), se sugiere una aparente disminución de la velocidad de reacción. Por otra parte, la intensidad de los picos de ZrO_2 sufren una drástica disminución cuando T_{calc} varía desde 900 a 1300°C, seguido de un leve incremento a T_{calc}=1400°C. Los estudios fueron realizados manteniendo condiciones isotérmicas a 1100, 1200 y 1300°C durante 0,5, 1, 2, 4, 8 y 16 h. En las tres temperaturas, el aumento de t_{calc} hasta 4 h conduce a un marcado aumento de la intensidad de las líneas características del NASICON, mientras que las correspondientes a $mZrO_2$ disminuyen. Un "plateau" es observado a valores altos de t_{calc}, lo que sugiere que un equilibrio está siendo alcanzado. La utilización de polvos altamente reactivos de ZrO_2 tetragonal (termodinámicamente inestable a baja temperatura) mejoró claramente la extensión y la cinética de reacción a temperaturas moderadas, conduciendo a la formación de un producto monofásico.

Palabras clave: NASICON, microestructura, reacción de estado sólido, XRD.

1. INTRODUCTION

The existence of fast ionic transport of Na^+ ions in $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ was reported in 1976 by Hong et al. [1] and Goodenough et al. [2]. These materials are generally referred to as NASICON, **Na**trium **s**uper *i*onic **con**ductors. The best ionic conductivity values are obtained for $1.8 < x < 2.2$ [3] in which the structure retains monoclinic symmetry. Other values of x lead to a considerably less conductive rombohedral symmetry [3,4].

Since the early works on this system, the processing of ceramics was considered of major importance for the application of all the potential of such fast ion conductor. Impedance spectroscopy studies have shown that the grain boundary contribution to the overall resistance of the material may be significantly larger than the contribution of the grain [5-11]. Moreover, its amplitude is strongly dependent on the processing conditions, in particular when the ceramics are sintered at temperatures higher than about 1230°C. In these conditions, the degradation of the grain boundary conductivity is interpreted as a direct consequence of

segregation of a monoclinic zirconia ($mZrO_2$) second phase at the grain boundaries, probably following Na and P volatilisation [5]. Therefore, the strategies to obtain NASICON ceramics with better performance have been based on the use of different precursors (mainly for Zr), either by sol-gel methods [6,7] or the classical ceramic route [8,9], with favourable reaction kinetics at low temperature. Successful results were indeed obtained with both approaches [6-9]. The reason for such improvement is likely to be related to the higher reactivity of the alternative Zr precursors. However, it remains unclear whether the $mZrO_2$ is exclusively segregated after P or Na losses at high temperature or, on the other hand, it is inherent to equilibrium. In fact, the complexity of the $Na_2O-P_2O_5-ZrO_2-SiO_2$ phase diagram was previously noticed by von Alpen et al. [12] whom have proposed the formula $Na_{1+z}Zr_{2-y}Si_xP_{3-x}O_{12}$ with z-x-4y=0. This work represents an attempt to clarify the roles of processing route and zirconium precursor on the formation and consumption of $mZrO_2$ during the processing of NASICON by conventional ceramic processes.

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2. EXPERIMENTAL PROCEDURE

This study is focused in the formation reaction of nominal $Na_3Zr_2Si_2PO_{12}$ from amorphous SiO_2 (Merck), $Na_3PO_4 \bullet 12H_2O$ (Merck) and a highly reactive $mZrO_2$ (Riedel -de- Haën) powder fabricated by a gel-combustion method. The precursors were intimately mixed in a polymeric container using zirconia balls and ethanol as suspending agent, dried at 60°C and pressed into disks with 1 cm in diameter at 59 MPa. These conditions were adjusted to ensure the best possible contact between the reactants particles. The reactivity studies consisted of two sets of experiments to evaluate separately the effect of temperature (T_{calc}) and time (t_{calc}) of calcination. In a first series of experiments, t_{calc} was of 2 h for T_{calc} fixed at 900, 1000, 1100, 1150, 1200, 1250, 1300 and 1400°C. In a second series, the effect of t_{calc} was tested for 0.5, 1, 2, 4, 8 and 16 h at three different levels of T_{calc} (1100, 1200 and 1300°C). In all experiments, the heating and cooling rates were fixed at 18 K/min. The maximum T_{calc} value is limited by the $Na_3Zr_2Si_2PO_{12}$ liquidus temperature which is reported in the range 1280 to 1310°C [1,2,5].

A second type of materials with nominal $Na_3Zr_{1.88}Y_{0.12}Si_2PO_{11.94}$ composition (NASICON-Y) was prepared following exactly the same procedure but replacing the $mZrO_2$ precursor by a very fine and reactive $(ZrO_2)_{0.97}(Y_2O_3)_{0.03}$ powder (Tosho Co.). A detailed description of the processing and characterisation of the structure, microstructure, stability and electrical properties of this compound has been reported elsewhere [9-11].

After sintering, the ceramic disks were crushed for subsequent analysis by X-ray diffraction (XRD). The patterns were obtained with a PW 3710 Philips diffractometer operating at 40 kV and 40 mA using Cu-Kα radiation. Data were collected in the 2θ range between 20° and 40° in step-scanning mode with a width of 0.02° and collecting counts over 5 s. The fraction of the $mZrO_2$ and $Na_3Zr_2Si_2PO_{12}$ phases is assumed to be proportional to the area of the corresponding diffraction maxima calculated as the peak height times the peak width measured at half height. From now on, $Na_3Zr_2Si_2PO_{12}$ will be referred to as NASICON. The microstructural features were analysed with a Philips 515 scanning electron microscope equipped with an energy dispersive spectroscopy (EDS) detector.

3. RESULTS AND DISCUSSION

3.1. Scanning electron microscopy

The SEM micrographs shown in Figs. 1A and 1B were obtained with samples calcined at 1100°C for 0.5 h and 8 h, respectively. It can be seen that at such low T_{calc}, and for the shorter t_{calc}, the morphology of the reactants mixture presents a glassy aspect (Fig. 1A) which suggests the formation of liquid. In fact, the formation of liquid in the $2Na_2O\square P_2O_5$ - $9Na_2O\square 2P_2O_5\square 6SiO_2$ - SiO_2 compatibility triangle is expected to occur from temperatures as low as 950°C [13]. On the other hand, the reaction of ZrO_2 with this liquid leading to the formation of Zr silicates or phosphates is also highly probable at this temperature [13]. Indeed, increasing t_{calc} up to 8 h leads to significant changes in the microstructure, in which large grains of a crystalline phase of composition similar to NASICON (according to EDS) are clearly observed (Fig. 1B). The size of these crystallites significantly increases with increasing the calcination temperature (Figs. 1C and 1D). The appearance of a new crystalline phase identified as pure zirconia was detected for T_{calc} values close to 1300°C or higher (Fig. 1D). These zirconia crystallites are perhaps the result of the precipitation of $mZrO_2$ due to Na and P volatilisation during the high temperature treatments. The identification of the phases formed was performed by XRD.

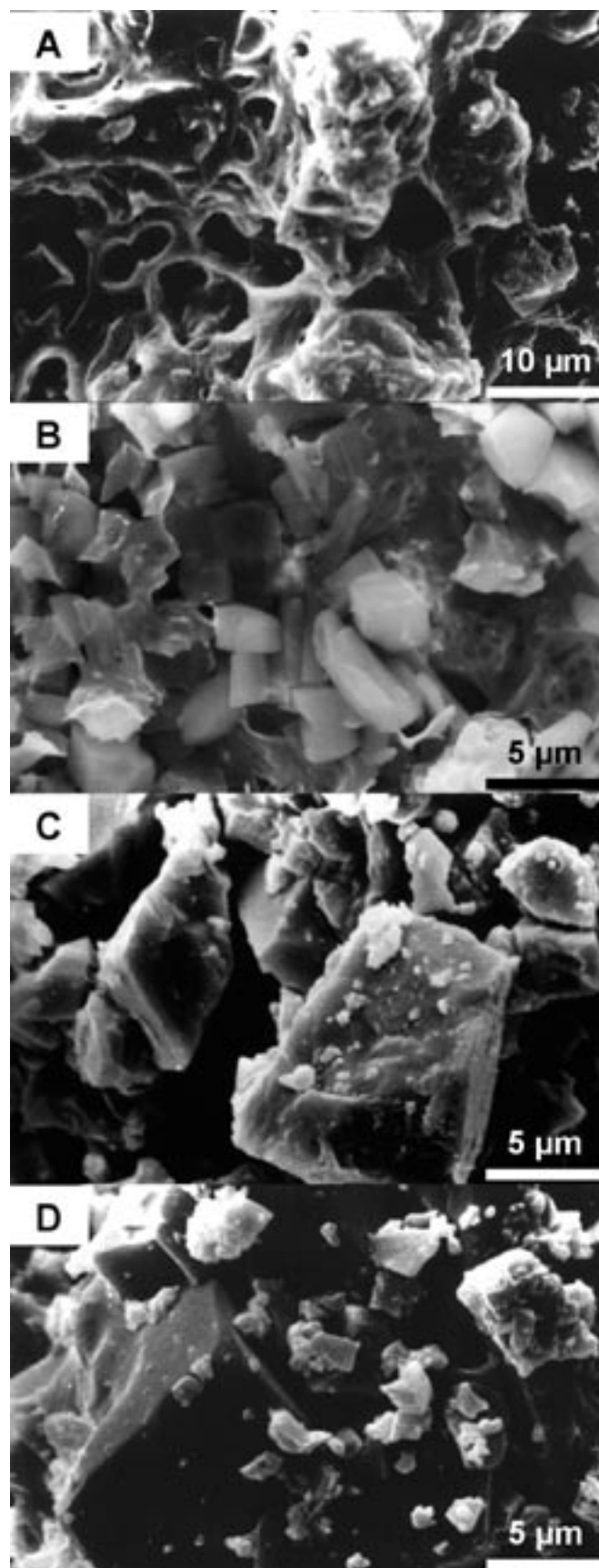Fig. 1. SEM micrographs of NASICON precursors mixtures calcined in different conditions: A) 1100°C, 0.5 h; B) 1100°C, 8 h; C) 1200°C, 8 h; D) 1300°C, 8 h.

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3.2. X-ray diffraction

The powder XRD patterns collected on crushed ceramic samples, presented in a limited 2θ range from 27 to 29 degrees, show the evolution, with the processing conditions, of the NASICON (400) and (22$\bar{2}$) reflections and also the mZrO$_2$'s (11$\bar{1}$). Fig. 2 shows the patterns obtained with samples calcined at different temperatures for 2 h. It can be seen that NASICON is not formed when T$_{calc}$ is 1000°C or lower. At 1100°C, the onset of low intensity NASICON peaks indicate the early stages of the formation reaction that is significantly enhanced when T$_{calc}$ increases up to 1200 and 1300°C. This observation fully agrees with the SEM micrographs and further confirms the EDS indication that the observed crystallites have a composition similar to that of NASICON. For higher temperatures, there is an apparent decrease of the reaction rate for NASICON formation, particularly clear when comparing the spectra corresponding to T$_{calc}$ = 1300 and 1400°C. On the other hand, the intensity of the (11$\bar{1}$) reflection of mZrO$_2$ suffers a drastic decrease when T$_{calc}$ varies from 900 to 1300°C, followed by a slight increase for T$_{calc}$=1400°C. It is now clear that the small white crystallites formed at higher T$_{calc}$ (Fig. 1D), previously identified as nearly pure zirconia according to EDS, are indeed pure mZrO$_2$.

The overall process involves reaction of zirconia with other components at relatively low temperature (< ca. 1100°C) forming a transient phase, probably vitreous, with a composition similar to that of NASICON. The formation of NASICON is expected to start in the range 1000-1100°C and is strongly enhanced at higher temperatures (1200-1300°C). Significant fractions of Na and P may be lost by volatilisation [9] at temperatures above 1300°C, and the structure tends to release the Zr^{4+} cations that precipitate as the oxide. Thus, the formation of crystalline NASICON occurs in a relatively narrow temperature range and should be strongly influenced by the slow kinetics. Therefore,

the effect of the calcination time was studied in more detail for T$_{calc}$ values between 1100 and 1300°C. It should be noticed that formation of NASICON at temperatures out of this range cannot be detected or is affected by the volatilisation of Na and P. The powder XRD patterns obtained with samples calcined under these conditions are shown in Fig. 3. The behaviour is similar for all temperatures with two main features deserving attention: i) the increase of t$_{calc}$ up to ca. 4 h leads to a significant increase in the intensity of the NASICON reflections while that of mZrO$_2$ decreases; ii) a plateau is apparent for higher t$_{calc}$ values, suggesting the establishment of an equilibrium between the two phases. The figure is more clearly evidenced on plots of the diffraction peak area as a function of t$_{calc}$ (Fig. 4).
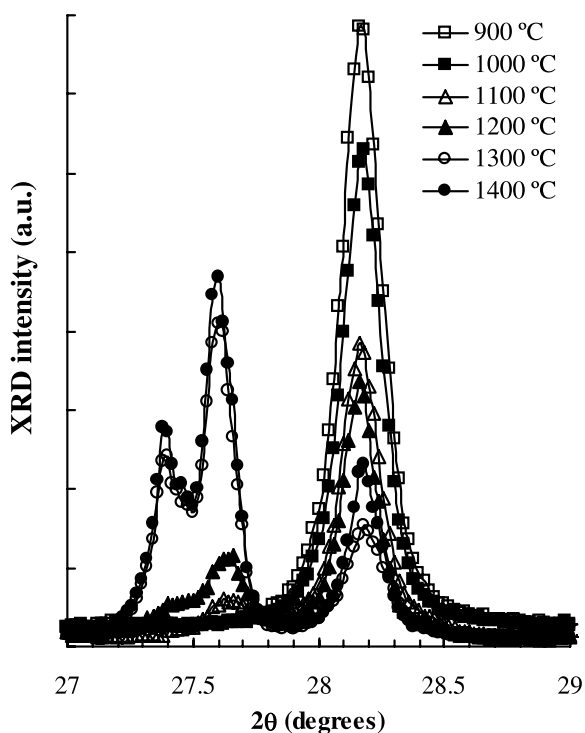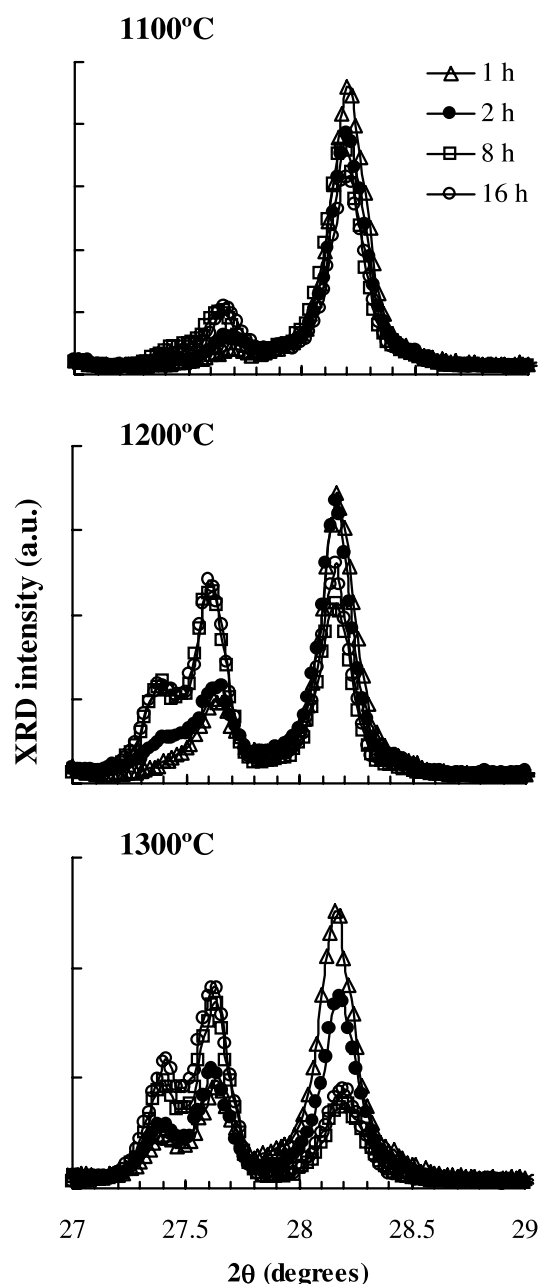

Fig. 2. XRD patterns of NASICON precursors mixtures calcined at different temperatures during 2 h. The diffraction maxima at 27.4 and 27.6° correspond to the (400) and (22$\bar{2}$) NASICON reflections while the peak at ca. 28.2° is ascribed to the mZrO$_2$ (11$\bar{1}$).

Fig. 3. XRD patterns of NASICON precursors mixtures calcined at 1100, 1200 and 1300°C for different periods of time. The diffraction maxima at 2θ = 27.4 and 27.6° correspond to the (400) and (22$\bar{2}$) NASICON reflections while the peak at ca. 28.2° is ascribed to the mZrO$_2$ (11$\bar{1}$).
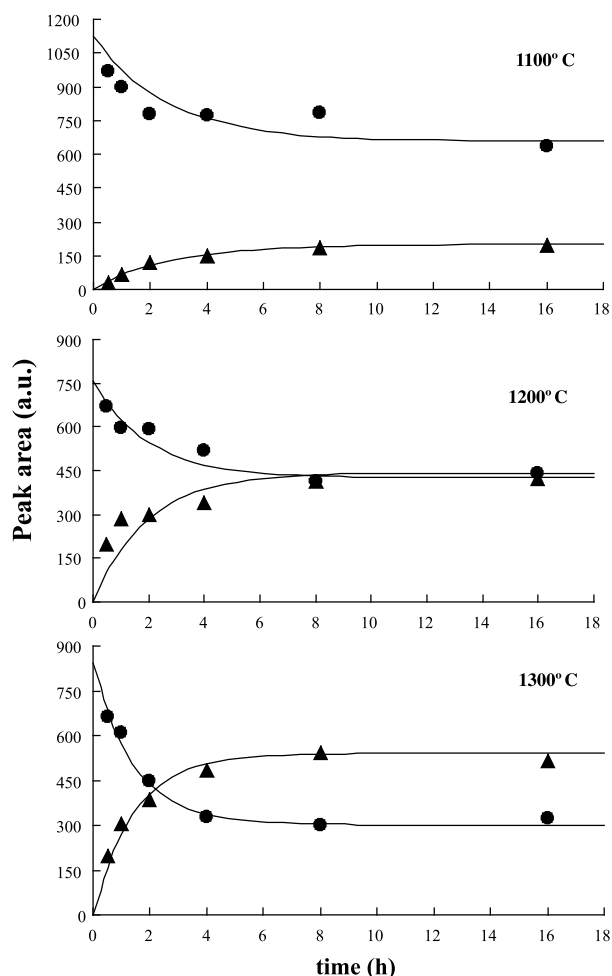
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Fig. 5. XRD patterns of NASICON-Y precursors mixtures calcined for 8 h at 1100°C.

Fig. 4. Evolution of the area of the (▲) NASICON(22$\bar{2}$) and (●) ZrO$_2$ (11$\bar{1}$) peaks for precursors mixtures calcined for different periods of time at 1100°C, 1200°C and 1300°C. The lines are a guide to the eye.
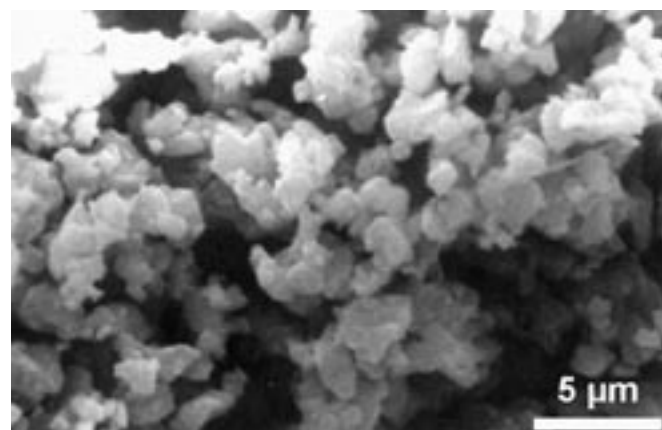
Fig. 6. SEM micrograph of NASICON-Y precursors mixtures calcined at 1100°C for 8 h.

The discussion of equilibrium in reactions between powders is always a delicate matter since the reactants may be locally heterogeneous and factors such as the particle morphology and size are of importance. Several models were developed to derive reaction rates taking into account these effects [14]. However, the application of such models to the present case is difficult since it is impossible to determine the fraction of liquid, which should be fairly high for low T$_{calc}$ and t$_{calc}$, according to Fig. 1A.

3.3. Effect of the zirconium precursor

It has been demonstrated that the material with nominal composition Na$_3$Zr$_{1,88}$Y$_{0,12}$Si$_2$PO$_{11.94}$ (NASICON-Y) obtained using a fine and very reactive (ZrO$_2$)$_{0.97}$(Y$_2$O$_3$)$_{0.03}$ powder as zirconium precursor [9-10]. Powders of NASICON-Y were obtained under exactly the same processing conditions as for NASICON. A typical powder XRD spectrum obtained for a NASICON-Y sample calcined at 1100°C for 8 h is shown in Fig. .5. It can be seen that, contrary to NASICON, NASICON-Y may be obtained at 1100°C without apparent vestiges of mZrO$_2$. Moreover, the microstructure of the NASICON-Y powder (Fig. 6) suggests that the level of crystallisation is considerably higher than for NASICON (Fig. 1B).

It is well know that the 3 mol% yttria in (ZrO$_2$)$_{0.97}$(Y$_2$O$_3$)$_{0.03}$ stabilises the zirconia tetragonal polymorph at room temperature, otherwise
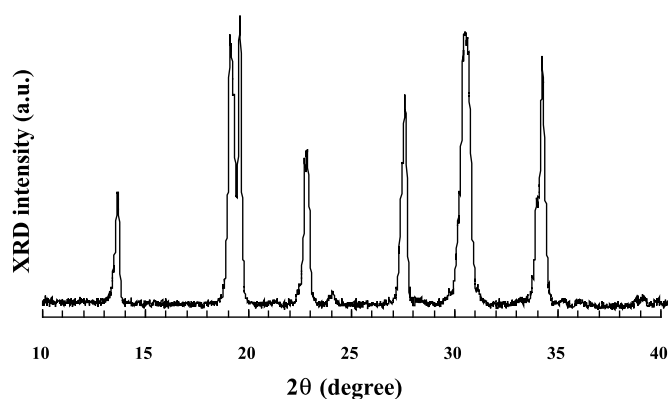
existing only between 1100 and 2370°C [15]. The lower limit of the tetragonal ZrO$_2$ temperature stability range actually corresponds to the temperature at which the NASICON starts to form. The clear improvement of the overall reaction kinetics and extension at moderate temperatures, achieved by using the highly reactive (ZrO$_2$)$_{0.97}$(Y$_2$O$_3$)$_{0.03}$ powder, should thus be due to the thermodynamic instability of this precursor at low temperature. Under the aforementioned hypothesis of thermodynamic equilibrium, the boundary between the NASICON + ZrO$_2$ immiscibility and pure NASICON domains should be shifted to lower temperatures or higher zirconia fraction when this precursor retains the tetragonal structure at low temperature.

4. CONCLUSIONS

The analysis of the phase composition by XRD of samples calcined at temperatures ranging from 900 to 1400°C suggests that the overall reaction is likely to involve reaction of zirconia with other components at relatively low temperature (< ca. 1100°C) forming a transient phase, probably vitreous, with a composition similar to NASICON. Extensive formation of NASICON was only observed in the range 1100-1300°C. At higher temperatures, the precipitation of monoclinic zirconia occurs probably due to volatilisation of significant amounts of Na and P. These results are fully consistent with SEM observations.

The reaction kinetics was studied at 1100, 1200 and 1300°C for periods of time up to 16 h. XRD results showed that reaction is never completed. The intensity of the reflections of NASICON increases significantly for the first 4 h of thermal treatment and reaches a constant value for longer calcination times. The zirconia peaks show an inverse trend, decreasing for short t_{calc} and the subsequent plateau. This behaviour may be interpreted as the result of thermodynamic equilibrium between the NASICON and $mZrO_2$ phases, which may also involve a liquid phase. The boundary between the immiscibility and pure NASICON domains is apparently shifted to lower temperature or higher zirconia fraction when tetragonal zirconia is used as Zr^{4+} precursor, since single phase NASICON could, in this case, be obtained using the same processing conditions.

ACKNOWLEDGEMENTS

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