Journal of the European Ceramic Society 22 (2002) 1995–2000

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NMR and XRD study of the influence of the P precursor in sol-gel synthesis of NASICON powders and films

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Received 20 September 2001; received in revised form 3 December 2001; accepted 8 December 2001

Abstract

NASICON ($Na_3Zr_2Si_2PO_{12}$) has been prepared by a sol-gel route. The progress of the reaction in the liquid has been monitored by means of ^{31}P NMR spectroscopy. The dependence of phase formation and sintering behaviour of films and powders on sol-gel reactions and heat treatments was investigated. X-ray diffraction measurements showed the formation of monoclinic NASICON phase from 800 °C for powders and from 900 °C for films together with free ZrO_2. An almost pure NASICON phase was observed in powders calcined at 1000 °C. Sintered pellets showed densities up to 98% of theoretical value. The microstructure of the samples was analysed by scanning electron microscopy. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Films; Ionic conductivity; Microstructure-final; NASICON; Sol-gel processes

1. Introduction

Sodium superionic conductors (NASICON) are solid solutions of sodium zirconium phosphate and sodium zirconium silicate. NASICON compounds have a general formula $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ with $0<x<3$ and are among the best tridimensional ionic conductors. They can be used in many electrochemical devices, such as sensors and batteries. For mass production at low cost, or to miniaturize such electrochemical devices, it is necessary to produce solid electrolytes as thin films. In fact for the realization of efficient devices it is necessary to produce thin electrolytes in order to obtain high current densities between the electrode surfaces.

After the first study by Hong[1] many attempts were made for producing glass phases and ZrO_2 free NASICON ceramics both by solid state reaction and wet chemical synthesis.[2–5]

It has been demonstrated that sol-gel technique can offer a good alternative synthesis route for NASICON powders and a convenient way for deposition of NASICON thin films. Yoldas and Lloyd[6] developed an all alkoxides sol-gel synthesis for producing zirconia free rhombohedral NASICON at room temperature. Since then many studied have been reported on alkoxides sol-gel synthesis of NASICON. Perthuis and Colomban[7] sintered rhombohedral NASICON discs at temperature lower than 1100 °C and high dense (higher than 95%) discs of monoclinic NASICON (containing ZrO_2 contamination) at temperature higher than 1100 °C. Høj and Engell[8] studied the formations of glass phases for different compositions of NASICON. Gasmi et al.[9] investigated the effect of hydrolysis and the role of complexing reagent on the crystallization and sinterability of NASICON. The effect of the hydrolysis on the NASICON structure was also investigated by Di Vona et al.[10] Sol-gel synthesis of NASICON powders from aqueous solution[11] or using citrates[12] were also reported. NASICON thin films have already been synthesized by sol-gel through hydrolysis and condensation of alkoxides,[13] or using a aqueous complex precursor.[14] Control of the sol-gel reactions is however very difficult in a complex system such as NASICON in which four different precursors with different hydrolysis and condensations rates are involved. A non-hydrolytic route, in which, for examples, metal alkoxides and chlorides react together, avoids the problems connected with the different hydrolysis rates of conventional sol-gel

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PII: S0955-2219(01)00536-2

process, allowing a better structural homogeneity of the sol.[15] Recently Di Vona et all.[16] demonstrated that the non-hydrolytic route can be successfully applied to the synthesis of NASICON powders.

In this work we report the synthesis and the characterization of $Na_3Zr_2Si_2PO_{12}$ thin films and powders obtained through the reaction of alkoxides and chlorides. The progress of the reaction in the liquid has been monitored by means of ^{31}P NMR spectroscopy and the structural thermal evolution of both films and powders was investigated.

2. Experimental

NASICON ($Na_3Zr_2Si_2PO_{12}$) powders and films were synthesized by the sol-gel method. Tetraethoxysilan ($Si(OEt)_4$), zirconium (IV) butoxide (80 wt.% in butanol) ($Zr(OBu)_4$), sodium ethoxide (NaOEt), phosphorous pentachloride (PCl_5) (Aldrich), zirconium tetrachloride ($ZrCl_4$) (Fluka) and absolute ethanol (Ashland Chemical) were used. Each step of the sol preparation was conducted at room temperature.

In Fig. 1 is reported the flow chart for the solution preparation. In sol S1, $Zr(OBu)_4$ and PCl_5 (1:1 molar ratio) were allowed to react for 15 min, than EtOH ($EtOH:PCl_5 = 40:1$) was added.

In sol S2, TEOS and $ZrCl_4$ (2:1) were also stirred for 15 min before adding EtOH ($EtOH:ZrCl_4$ 82:1). S1 and S2 were then mixed to give a clear solution (sol S3). The addition of NaOEt (NaOEt: $ZrCl_4$ 7:1) to sol S3 give rise to a NaCl precipitate, due to the reaction with chloride ions present in sol S3. NaOEt was added until the complete precipitation of NaCl. The precipitate obtained was collected by spin-drying. NaOEt was further added to the Cl^- free solution to reach the right stoichiometric quantity. The final sol was clear and stable for many months.

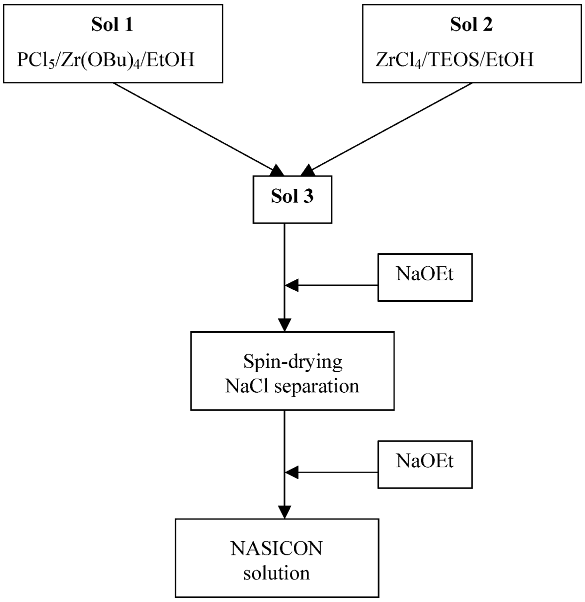

Fig. 1. Flow chart for the synthetic route of the NASICON solution.

Single and multilayer films were deposited from fresh and aged (72 h) sols on silicon or alumina substrate by dip-coating at 30% R.H. Multilayer films were obtained by heating each layer at 500 °C for 15 min. The samples obtained were put directly in the preheated furnace and fired in air for 1 h at different temperatures from 600 to 1200 °C.

Powders were obtained from solutions by evaporation in air under room temperature for 1 week (slow drying) or at 60 °C for 1 day (fast drying). Powders were calcined at temperatures from 600 to 1200 °C for 1 h in air.

Powders calcined at 1100 °C were subjected at isostatic pressing to obtain pellets 1.9-cm-diameter ($p = 100$ atm). Pellets were sintered in air at 1150 °C for 12 h (heating rate of 5 °C/min).

NMR spectra were recorded on a Brüker AM 400 spectrometer. ^{31}P chemical shifts are given in ppm from external H_3PO_4 (85% w/w).

The thermal decomposition behavior of the complexes was studied by thermogravimetric and differential thermal analyzses (TG/DTA), performed in flowing air with a heating rate of 10 °C/min.

Thin films, powders and pellets were analyzed by X-ray diffraction (XRD) using a Philips diffractometer with a glancing angle configuration. CuK_α, operating at 40 KV and 50 mA, was used as the radiation source. The average crystallite size was calculated from the Scherrer equation after fitting the experimental profiles using the method described in Ref. 17.

The microstructure and chemical composition of sintered pellets and films were analyzed by scanning electron microscopy (SEM) equipped with an energy dispersive X-ray detector.

The density of sintered pellets was measured by the Archimedes principle in distillate water at room temperature.

A dilatometric study was conducted on sintered samples with a heating rate of 2 °C/min. The dilatometer was calibrated using a known α-alumina polycrystalline standard.

3. Results and discussion

The progress of the reaction has been monitored by means of ^{31}P NMR spectroscopy. Fig. 2a shows the spectrum of sol S1. The chemical shift values observed indicate that the phosphorous atoms are present in four-co-ordinated compounds containing P–O double bonds and not as a simple five co-ordinated species since these latter are characterized by very large negative shifts (ca. −70 ppm).[18] The presence of numerous broad resonances indicate

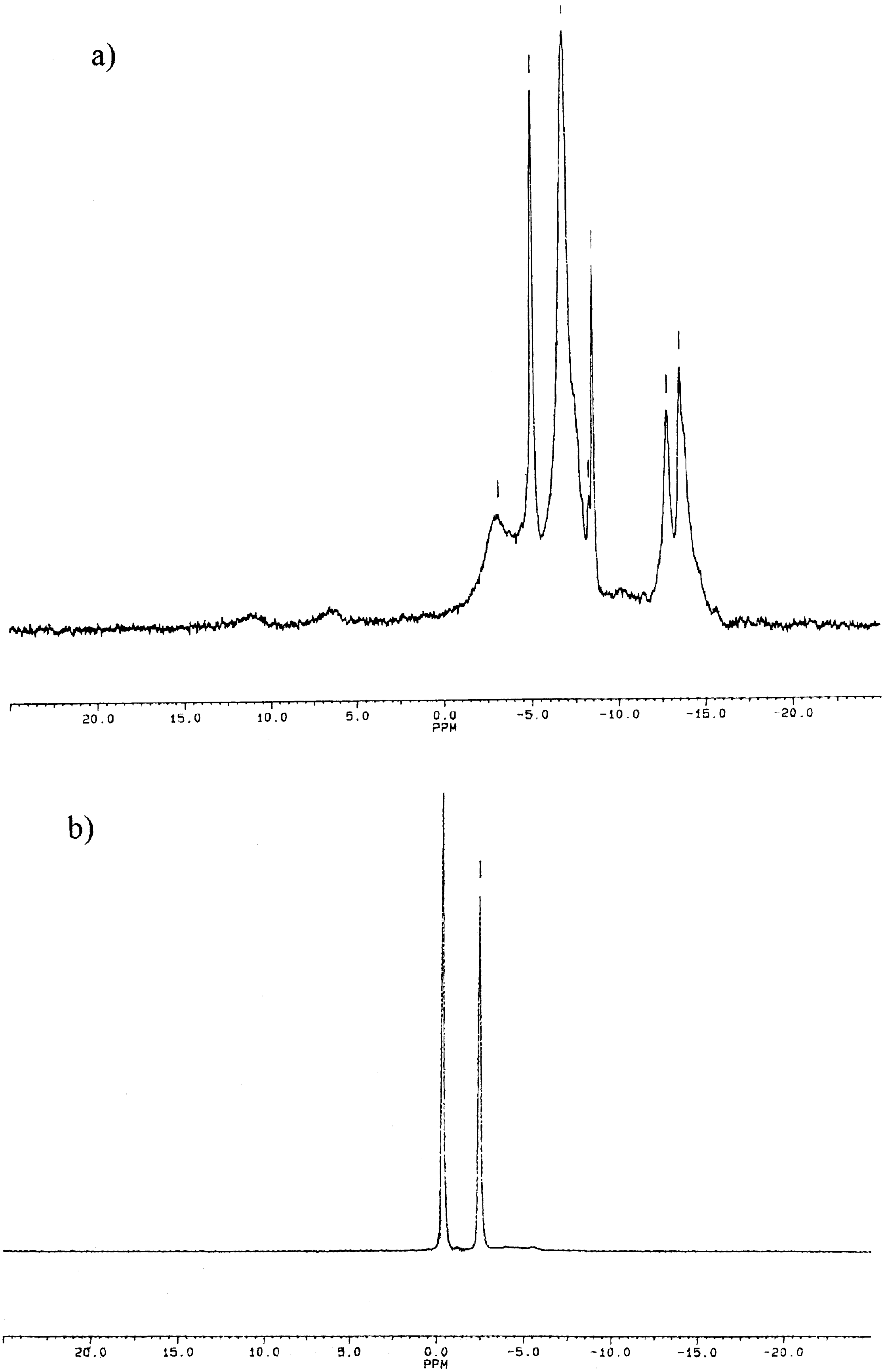

Fig. 2. (a) ^{31}P NMR spectrum of the mixture PCl_5 and $Zr(OBu)_4$ in ehtyl alcohol (sol 1 of flowchart); (b) ^{31}P NMR of the final solution.

that the P atom is present in different environments. The chemical shifts values are consistent with the formation of species containing the –(P–O–Zr)– unit.[16] The formation of such units might be due to the reaction of PCl_5 with $Zr(OBu)_4$ through the following non-hydrolytic reaction:[19]

$$M - OR + Cl - PCl_4 \rightarrow M - O - PCl_4 + RCl.$$

The large line-width of the resonances is consistent with the formation of a polymeric network but does not allow to observe any ^1H–^{31}P J coupling that would give indications on the presence and/or nature of alkoxy groups directly bound to phosphorous.

In solution S2, in order to promote a non hydrolytic reaction, TEOS and $ZrCl_4$ were allowed to react before adding EtOH.

The addition of sol S2 to sol S1 does not cause substantial variations of the spectrum. Any reaction occurring between the two precursors solutions must then occur far away from the phosphorous center.

When NaOEt is added to the reaction mixture the ^{31}P spectrum recorded shows a dramatic change (Fig. 2b). The sharp resonances observed, the lack of any J coupling and the chemical shift values measured are consistent with the formation of phosphate ions with different degrees of protonation. In the very basic solution obtained the presence of traces of water originating from the atmosphere are sufficient to initiate hydrolysis of the precursors.

In order to clarify the effect of calcination temperature, TG–DTA measurements were carried out for a xerogel powder obtained from the slowly dried solution. As shown in Fig. 3, large mass losses of the sample were observed at temperatures between 50 and 500 °C, accompanied by an endothermic peak around 150–200 °C due to the evaporation of physiosorbed water or residual solvent and an exothermic peak between 350–500 °C due to the removal of a residual organic group.

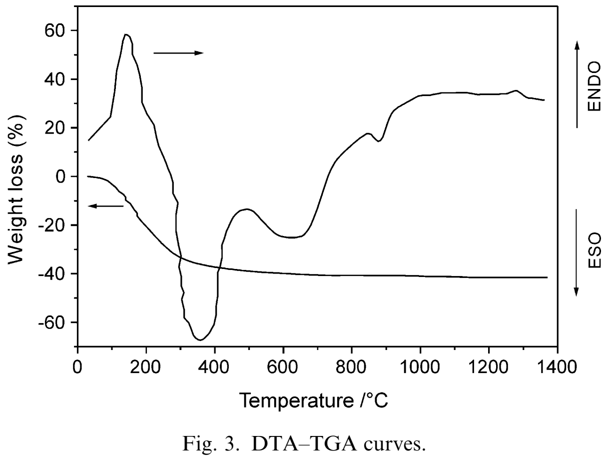

Fig. 3. DTA–TGA curves.

The exothermic peaks at 640 and 890 °C, not accompanied by weight losses, are ascribed to the crystalline ZrO_2 and NASICON phase formation, respectively. XRD analyses performed on powder heated with the same schedule confirmed these behaviors. The small endothermic peak between 1200 and 1300 °C is assigned to the compound melting in agreement with previously reported results.[20]

Fig. 4 shows the XRD spectra of powders obtained at room temperature and calcined at different temperatures. Tetragonal ZrO_2 (ICDD 17-923) crystallizes at 700 °C, while monoclinic $Na_3Zr_2Si_2PO_{12}$ (ICDD 35-412) was present from 800 °C. Traces of $Na_2ZrSi_2O_7$ (ICDD 39-0209) were found in powders heated between 800 and 1000 °C as already observed in other sol-gel systems.[21] Higher content of $Na_2ZrSi_2O_7$ was observed in powder obtained by fast evaporation. The formation of this phase can be due to an evaporation of phosphorous during the drying step, accentuated by a faster evaporation step. NMR spectra of the final sol revealed the formation of phosphate ions with different degrees of protonation which can easily evaporate. A slow drying can favor the reaction of phosphate ions with alkoxide[22] inhibiting the phosphorous evaporation. Moreover hydrolysis of phosphorous butoxide formed by the reaction of metal chlorides with the alcohol[23] contained in the zirconium precursor can't be excluded. In addition other authors[6,10] reported that a slow hydrolysis favors the formation of more pure NASICON powders.

Powders calcined at 1200 °C showed the presence of monoclinic $Na_3Zr_2Si_2PO_{12}$ and traces of monoclinic ZrO_2 (ICDD 37-1484), probably formed by the transformation of tetragonal ZrO_2. The disappearance of the sodium zirconium silicate phase can be due to its melting and formation of a glassy phase. In fact a very weak glassy halo pattern can be seen in the spectra of powder treated at 1200 °C (Fig. 4).

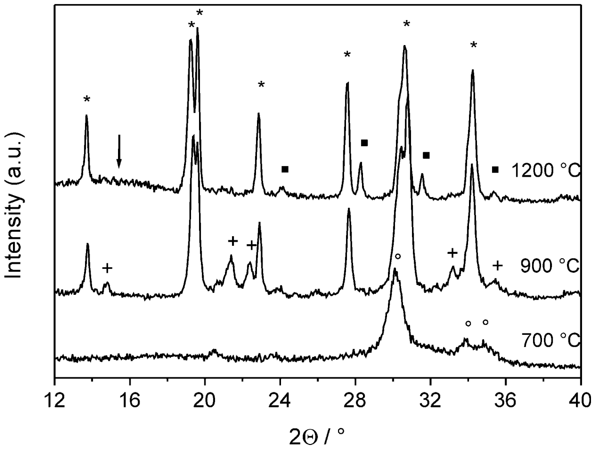

Fig. 4. XRD spectra of powders heated at different temeratures. The following phases were detected: NASICON (*), tetragonal ZrO_2 (°). monoclinic ZrO_2 (■) and $Na_2ZrSi_2O_7$ (+). A very weak glassy halo pattern (indicated by an arrow) can be seen in 1200°C heated samples.

The mean diameter of NASICON crystallites, estimated from the line-width of the <5, 1–3> reflection ($2\theta = 34.399°$), increases with heating temperature (from 16 nm at 900 °C to 19 nm at 1200 °C) indicating a crystal growth of the NASICON phase.

The XRD spectra of the sintered ceramic showed the presence of NASICON and traces of monoclinic ZrO_2. The densities of the sintered pellets are compared with the theoretical density calculated from the room temperature structure of the compound, 3.27 g/cm^3. Values up to 98% of theoretical was reached. Fig. 5 shows the microstructure of the sintered NASICON that consists of very fine (less than 5 μm) cubic grains, in agreement with the results reported on other sol-gel processed powders.[7] Instead, larger grains were obtained using solid state reactions.[3]

The dilatometric curve of a sintered sample is reported in Fig. 6. A dilatometric anomaly is present around 200 °C, due to the monoclinic/rhombohedral phase transition of crystalline NASICON, as already observed by others.[2,20] The evaluated thermal expansion coefficient ($\alpha^{(200-1000)} = 5.47 \times 10^{-6}$ C^{-1}) is also in agreement with the values previously reported for $Na_3Zr_2Si_2PO_{12}$ sintered at temperature higher than 1000 °C.[2,20]

Fig. 7 shows XRD patterns of NASICON thin films deposited on silicon substrates from aged solutions. Tetragonal ZrO_2 (ICDD 17-923) crystallizes at 800 °C, while monoclinic $Na_3Zr_2Si_2PO_{12}$ (ICDD 35-412) was present from 900 up to 1100 °C. At 1200 °C the only detected phase was monoclinc ZrO_2, probably due to decomposition of NASICON and formation of glassy phases, as already observed at 1300 °C for solid state sintered powders.[3] In fact no sodium lack was detected by X-ray microanalysis made on films heated at 1200 °C. The $Na_2ZrSi_2O_7$ phase (ICDD 39-0209) was clearly detected starting from 900 up to 1100 °C only in films deposited from fresh solution. As already pointed out for powders, the formation of this phase can be due to an evaporation of phosphorous during the drying step, which is faster in films than in powders. In aged sol the phosphate ions have more time to react with alkoxides inhibiting the phosphorous evaporation.

In Fig. 8 is reported a SEM micrograph of films deposited on Si and heated at 1100 °C. The surface of the layer is rough but no cracks seem to be present. A phase separation is clearly observed constituted by ZrO_2 grains; in fact no sodium was detected by X-ray microanalysis made on them. As observed by XRD, the

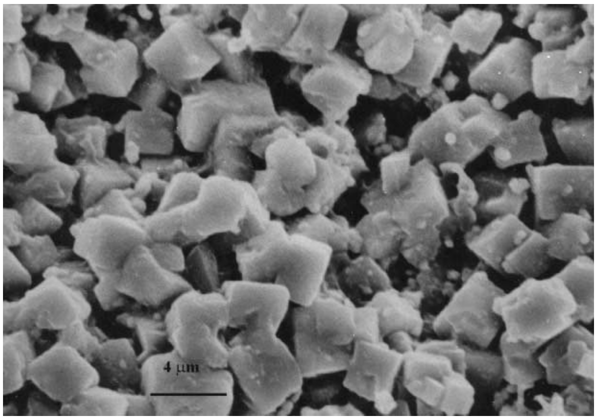

Fig. 5. SEM micrograph of a fragment of a pellet sintered at 1150°C.

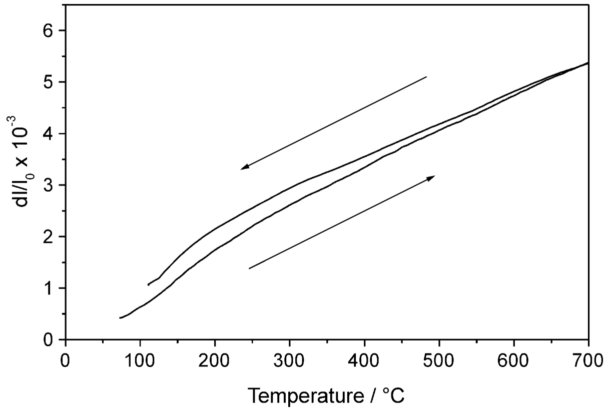

Fig. 6. Thermal expansion of NASICON sintered at 1150°C

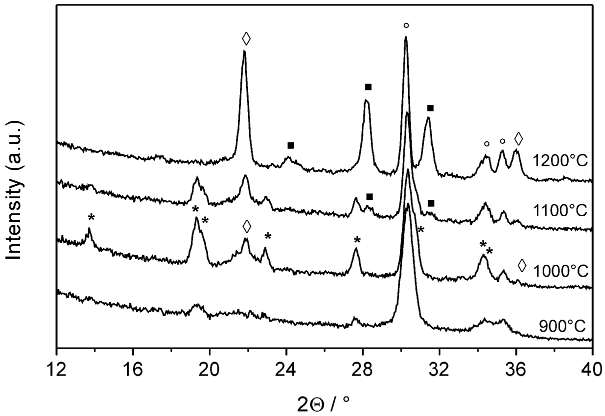

Fig. 7. XRD spectra of films deposited on Si and heated at different temperatures. The following phases were detected: NASICON (*), tetragonal ZrO_2 (°), monoclinic ZrO_2 (■) and $Na_2ZrSi_2O_7$ (+) the peaks indicated by (◇) are due to SiO_2 cristobalite formed on the substrate.

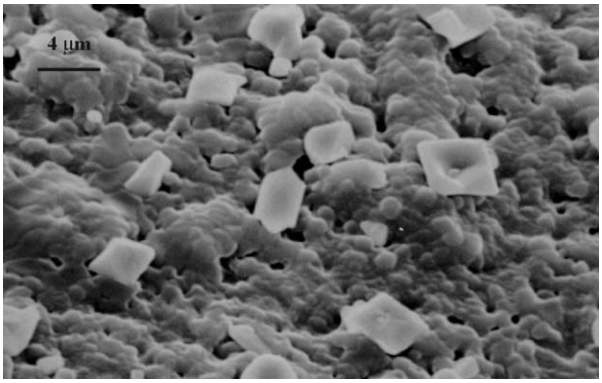

Fig. 8. SEM micrograph of a NASICON film deposited on silicon and heated at 1100°C.

NASICON phase starts to decompose at 1100 °C, while at 1200 °C only ZrO_2 phases are detected.

It is well known that the drying during the sol-gel film deposition is very fast leading to a different structural evolution of films respect to powders obtained from the xerogel, explaining the observed differences in the structural thermal evolution between the NASICON powders and films.

4. Conclusions

A new sol-gel synthesis of NASICON powders and films were developed through the reaction of alkoxides with chlorides like in a non-hydrolytic process.

Monoclinic $Na_3Zr_2Si_2PO_{12}$ powders were obtained at 900 °C. Well sintered (densities up to 98%) NASICON pellets containing only traces of monoclinic ZrO_2 were obtained at 1150 °C.

NASICON films deposited on silicon or alumina were obtained at 1000 °C. Films contain also ZrO_2 and $Na_2ZrSi_2O_7$ phases and decompose at 1200 °C. The formation of the $Na_2ZrSi_2O_7$ phase was attributed to the phosphorous evaporation during the deposition process.

The good results obtained for powders indicate that a better control of the sol-gel chemistry for inhibiting the phosphorous volatilization during the film deposition, will improve the composition of the NASICON layer.

Acknowledgements

This work has been supported by MURST.

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