Chem. Mater. **2001,** *13,* 141−144

Nonhydrolytic Synthesis of NASICON of Composition $Na_3Zr_2Si_2PO_{12}$: A Spectroscopic Study

Maria Luisa Di Vona,* Enrico Traversa, and Silvia Licoccia*

Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata,
Via della Ricerca Scientifica, 00133 Rome, Italy

Received July 12, 2000. Revised Manuscript Received October 23, 2000

NASICON ($Na_3Zr_2Si_2PO_{12}$) has been prepared by a nonhydrolytic route reacting $OP(OBu)_3$, $SiCl_4$, $Zr(O$*t*-$Bu)_4$, and NaO*t*-Bu in acetonitrile. The progress of the reaction was monitored by measuring ^{31}P and ^{13}C NMR spectra in the liquid phase and mass spectra of the reaction mixture. The spectroscopic analysis allowed optimization of the synthetic conditions. The thermal decomposition behavior of the precursor was studied by simultaneous thermogravimetric and differential thermal analysis. The NASICON precursor was heated to selected temperatures, and the resulting powders were analyzed by X-ray diffraction to check the formation of the NASICON phase. The powder obtained at 900 °C was almost pure, showing only traces of free zirconia.

Introduction

NASICON ($Na_3Zr_2Si_2PO_{12}$) is a solid electrolyte with very high Na^+ ionic conductivity,[1] suitable for use in electrochemical gas sensors.[2] Its conventional preparation through solid-state reactions leads to a material in which the NASICON phase is accompanied by a glassy phase and dissolved zirconia.[3,4] Several sol−gel routes have been developed to produce a pure phase.[5−8] Control of the preparative conditions is, however, hard to achieve in a complex system such as NASICON involving four different species. By following an all-alkoxides route, we obtained satisfactory results with respect to the elimination of undesired free zirconia, but the time for the synthesis was very long because it was necessary to slowly react the precursors with atmospheric moisture to avoid problems connected with the different hydrolysis rates of the precursors.[9]

Nonhydrolytic processes are very attractive alternative methods for the synthesis of multicomponent oxides.[10] Condensation reactions between different functionalities bound to different metal centers permit modulation of the reactivity of the various precursors, thus avoiding the problems connected with the control of different hydrolysis rates in conventional sol−gel preparations. Thus, for instance, metal halides can be reacted with metal alkoxides with elimination of alkyl halides. Among the advantages of such reactions is the volatility of byproducts that can be easily eliminated from the reaction mixture. The choice of solvent is almost unlimited in nonhydrolytic syntheses, so that reaction temperature and medium polarity can be varied to optimize the process.

In a preliminary paper, we have reported some new nonhydrolytic routes for the synthesis of NASICON.[11] The reactions have been monitored by means of heteronuclear NMR spectroscopy which has proved to be a powerful tool for the analysis of material precursors. Because the properties of materials are certainly related to their preparation methods, it is very important to control the synthetic procedures by means of rapid and easy measurements of some physicochemical characteristic of the precursors. The presence of nuclei which are routinely observed in NMR, such as ^{13}C and ^{31}P, make NASICON a very nice example where NMR in solution can be used to monitor the synthesis.

Different procedures have been considered, such as changing the precursors (alkyl derivatives, halides, alkoxides), their addition order, and the reaction solvent. The most promising results, in terms of homogeneous reactivity and characteristics of the final material obtained after thermal treatments of the precursors, have been obtained by using silicon halides with phosphorus, zirconium, and sodium alkoxides.

We now report an optimized nonhydrolytic procedure for the preparation of NASICON, studied by means of spectroscopic techniques, that leads to a high-quality material.

Experimental Section

All reagents (Aldrich) were reagent grade and were used without further purification. All of the preparation was carried out under N_2.

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10.1021/cm001128i CCC: $20.00

NASICON was prepared as follows: Tributyl phosphate ($OP(OBu)_3$, 0.36 mL, 1.3 mmol) was dissolved in anhydrous[12] CH_3CN (20 mL). Silicon tetrachloride ($SiCl_4$, 0.30 mL, 2.6 mmol) was added, and the solution was refluxed for 48 h. After the solution was cooled to 0 °C, zirconium(IV) *tert*-butoxide ($Zr(Ot\text{-}Bu)_4$, 1.0 g, 2.6 mmol) was added. The solution was slowly warmed to room temperature and kept stirring for 6 days. The preparation was completed by adding sodium *tert*-butoxide (NaO*t*-Bu, 0.37 g, 3.9 mmol) and leaving the mixture stirring at room temperature for 24 h. Sol−gel transition was observed after this period. The solvent was vacuum evaporated, and the residue was dried at 120 °C for 15 h and then comminuted in a ball mill.

Samples for NMR measurements were prepared following the above-described procedure, scaling the amount of the reagents in order to have a total volume of 2.7 mL and adding 0.3 mL of CD_3CN.

NMR spectra were recorded on a Bruker AM 400 spectrometer. ^{13}C chemical shifts are given in ppm from tetramethylsilane (TMS) and are referenced against solvent signals. ^{31}P chemical shifts are given in ppm from external H_3PO_4 (85% w/w).

Direct inlet mass spectra (electronic impact EI, 70 eV, source 200 °C, final probe temperature 400 °C) were recorded on a VG Quattro spectrometer.

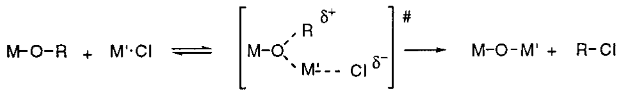
The thermal decomposition behavior of the precursor was studied by simultaneous thermogravimetric and differential thermal analysis (TG/DTA, model STA 409, Netzsch) with a heating rate of 10 K/min in air.

The NASICON precursor was heated at selected temperatures in the range from 600 to 900 °C for 2 h with a heating rate of 5 K/min. The phase evolution was investigated by X-ray diffraction (XRD) analysis using Cu Kα radiation.

Phosphorus atomic charge was calculated on the optimized geometries obtained by semiempirical methods (PM3) using the Hyperchem program.[13] Geometric optimizations were terminated when the energy difference among successive iterations was lower than $4.18\ 10^{-3}$ kJ/mol. Starting from PM3 geometries, we performed single-point ab initio computations using the Gaussian 98 system of programs.[14]

Results and Discussion

The reaction between metal alkoxides and metal chlorides is likely to occur through a mechanism that produces charge separation in the transition state:



Thus, the use of tertiary reaction centers and solvents with high dielectric constants should lower the energy of the transition state favoring the formation of products.

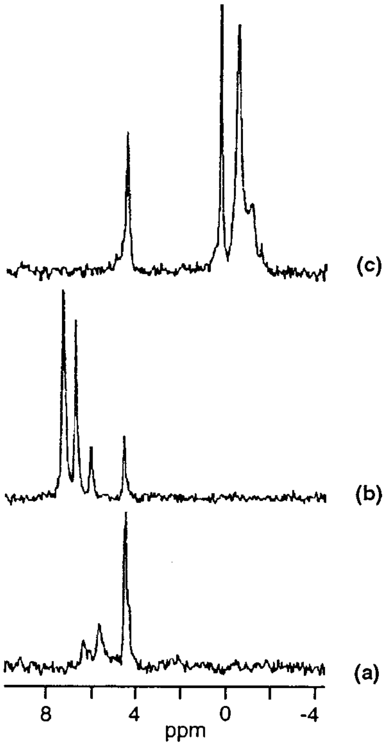


Figure 1. ^{31}P NMR of NASICON precursor solutions in 9:1 CH_3CN/CD_3CN: (a) $OP(OBu)_3 + SiCl_4$ after 24 h at reflux, (b) $OP(OBu)_3 + SiCl_4$ after 48 h at reflux, and (c) $OP(OBu)_3 + SiCl_4 + Zr(Ot\text{-}Bu)_4$.

The formation of NASICON starting from $OP(OBu)_3$, $SiCl_4$, $Zr(Ot\text{-}Bu)_4$, and NaO*t*-Bu in CH_3CN was studied, analyzing the reaction mixture spectroscopically. The choice of reactants was based not only on their relative reactivity but also on their commercial availability. Acetonitrile was chosen as the solvent because it is easy to obtain in an anhydrous form and it is not hygroscopic. Furthermore, it has a high dielectric constant ($\epsilon = 38$); it favors the formation of charged intermediates but has a relatively low coordination ability (DN = 10), so that it does not block, through coordination, sites available for polymerization reactions.[15]

The ^{31}P NMR spectrum of the mixture obtained by reacting $OP(OBu)_3$ and $SiCl_4$ in acetonitrile for 24 h is shown in Figure 1a. The spectrum shows an intense resonance at 4.3 ppm, resulting from unreacted tributyl phosphate, with some weaker deshielded resonances. Their intensity increases if the reaction is carried out for a further 24 h (Figure 1b). The downfield shift of the resonances can be attributed to the deshielding effect caused by substitution of alkyl groups by $-SiCl_3$, and their presence is indicative of the formation of a polymeric network containing the $-(P-O-Si)-$ unit. Despite the wealth of literature existing on ^{31}P NMR, no data have been reported on the solution spectrum of a similar polymer. Reports[16] on ^{31}P chemical shifts of products containing $OP(OSiMe_3)_n$ units bound to metal alkoxides or chlorides showed in fact the shielding effect of $-SiMe_3$ units which is, as expected, opposite to the deshielding effect observed in the present case where

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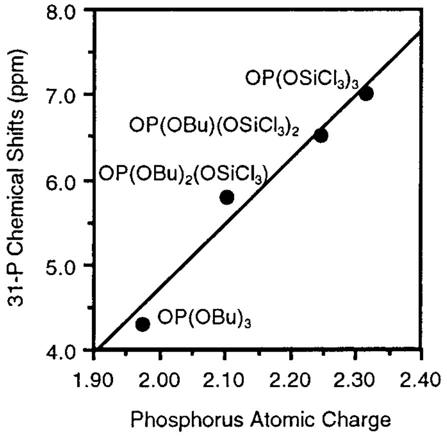


Figure 2. Least-squares fit of ^{31}P chemical shifts (ppm) of NASICON precursor solution [$OP(OBu)_3 + SiCl_4$] vs calculated P atomic charge.

the shifts are dominated by the presence of silicon-bound chlorides. Among the different factors that contribute to ^{31}P NMR chemical shifts, it is well-known that within a series of structurally similar compounds an increase in atomic charge on the P atom leads to a decrease in shielding.[17] A theoretical approach based on ab initio calculations with the RHF/LanL2Dz[18,19] basis set was used to determine the phosphorus atomic charge, calculated by Mulliken population analysis (MPA) for the series of compounds $OP(OBu)_3$, $OP(OBu)_2(OSiCl_3)$, $OP(OBu)(OSiCl_3)_2$, and $OP(OSiCl_3)_3$. Atomic charges are not quantum mechanical observables, and methods for their calculation are necessarily arbitrary. Therefore, it is not their absolute values that should be considered but only their variation within the series. Figure 2 shows the correlation obtained between the measured ^{31}P chemical shifts and the calculated charges. The good correlation obtained ($r^2 = 0.962$) supports the formation of the proposed structures.

Zirconium was then added to the reaction mixture as $Zr(Ot\text{-}Bu)_4$. A tertiary alkoxide was chosen to favor the formation of carbocationic species and hence the condensation reaction. The ^{31}P spectrum of the final mixture (Figure 1c) shows new resonances between 0 and −2 ppm which account for 90% of the total intensity of the spectrum, indicating a high degree of advancement of the reaction. Resonances are now shifted upfield as expected for a Zr-containing polymer because of the metal electropositive character. Again, no solution NMR data have been reported for similar species. However, in solid-state ^{31}P magic-angle spinning NMR most of the structures with phosphates linked to zirconium and silicon atoms give rise to shielded resonances, the chemical shift being more negative when a higher number of Si and Zr atoms are bound to the P−O unit.[5]

Figure 3 shows the ^{13}C spectrum of the reaction mixture. Together with the resonances of the residual alkoxide chains, those due to alkyl chlorides can be identified in the spectrum (n-BuCl: $\delta = 13.3$, 20.24, 34.9, 45.5; t-BuCl: $\delta = 34.2$, 67.9), confirming that the reaction basically initiates through the following sequence:

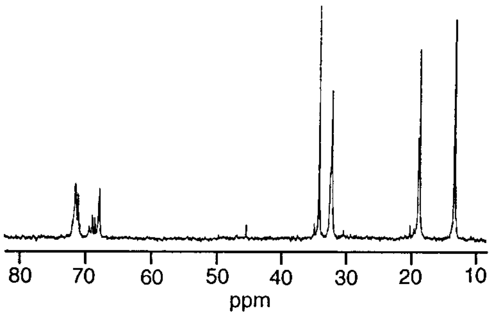
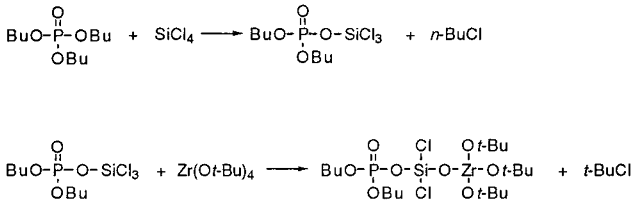


Figure 3. ^{13}C NMR spectrum of NASICON precursor solution in 9:1 CH_3CN/CD_3CN: $OP(OBu)_3 + SiCl_4 + Zr(Ot\text{-}Bu)_4$.



$$BuO{-}\underset{OBu}{\overset{O}{\overset{\|}{P}}}{-}OBu + SiCl_4 \longrightarrow BuO{-}\underset{OBu}{\overset{O}{\overset{\|}{P}}}{-}O{-}SiCl_3 + n\text{-}BuCl$$

$$BuO{-}\underset{OBu}{\overset{O}{\overset{\|}{P}}}{-}O{-}SiCl_3 + Zr(Ot\text{-}Bu)_4 \longrightarrow BuO{-}\underset{OBu}{\overset{O}{\overset{\|}{P}}}{-}O{-}\underset{Cl}{\overset{Cl}{Si}}{-}O{-}\underset{Ot\text{-}Bu}{\overset{Ot\text{-}Bu}{Zr}}{-}Ot\text{-}Bu + t\text{-}BuCl$$

The reaction will further proceed through condensation of other $SiCl_x$ units with butoxide groups bound to the different oligomers initially formed.

The group of resonances observed between 67 and 73 ppm are due to $-OCH_2$ and tertiary carbon atoms of the residual alkoxide chains. These carbon atoms are the closest to the reaction centers, and their chemical shift values are the most sensitive to structural variations. The presence of numerous resonances, their rather large line width and the sol−gel transition observed after 24 h are indicative of an extended polymeric network with numerous coordination environments.[9]

The progress of the reaction was also analyzed by mass spectrometry. Although it is seldom applied in materials chemistry, we have successfully used such a technique in a previous study on ceramic precursors.[20] Analysis of the fragmentation pattern can in fact give important information even when the molecular peak cannot be observed.

In the mass spectrum of $OP(OBu)_3$, the molecular peak (267 m/z) and a peak at 211 m/z resulting from loss of a butyl group can be identified (relative intensity 4:1). The same peaks are present in the spectrum of the residue obtained by rotary evaporation of the mixture prepared by reacting $OP(OBu)_3$ and $SiCl_4$ for 48 h, but their relative intensity is reversed (1:4), indicating that at least one butyl group was substituted by silicon. The peaks in the range 308−316 m/z can be attributed to a species containing a $-SiCl_2$ moiety bound to the 211 m/z fragment. Figure 4 shows the spectrum of the residue obtained by evaporating the reaction mixture after addition of $Zr(Ot\text{-}Bu)_4$. The peaks between 308 and 316 m/z are still present, but additional peaks around 454 m/z can be observed where $-OZr(Ot\text{-}Bu)$ substitutes a chlorine atom.

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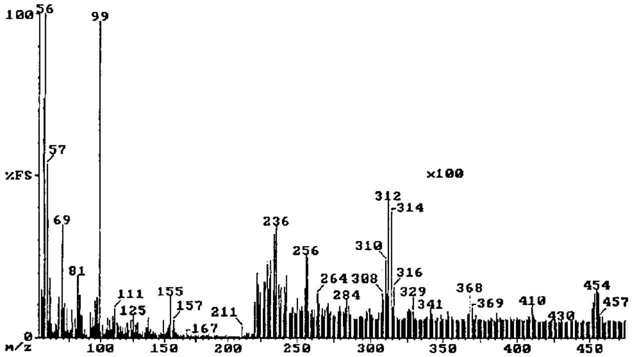

Figure 4. EI mass spectrum of NASICON precursor.

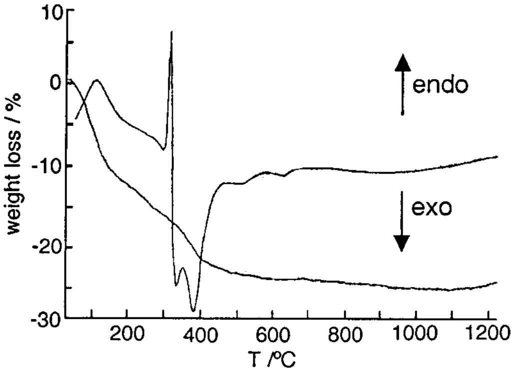

Figure 5. DTA and TG curves of the NASICON precursor.

The mass spectrometry results confirmed the NMR analysis of the reaction progress. The spectrum of a mechanical mixture of the three precursors was recorded, and the result was only the sum of the three individual spectra, thus verifying that the fragmentation pattern observed for the NASICON precursor did not derive from recombination reactions in the spectrometer.

Sodium ions are not expected to become part of the polymeric network; thus, the preparation was completed by adding NaO*t*-Bu.[5]

Figure 5 shows the TG/DTA curves for the NASICON precursor dried at 120 °C for 15 h. After the loss of physisorbed water (accompanied by an endothermic peak in the DTA curve), the weight loss started slowly in two steps and ended at about 600 °C. The two weight-loss steps were accompanied by a sharp endothermic peak with its maximum at about 300 °C, overlapped by an exothermic peak and by another exothermic peak with its maximum at about 380 °C. The endothermic peak can be attributed to the decomposition of residual chlorides which have not completely reacted in solution, and the exothermic peaks can be ascribed to combustion of organic residual chains. Weak exothermic effects were observed between 500 and 700 °C, probably resulting from crystallization phenomena.

The formation of NASICON was checked by performing XRD analysis that confirmed that crystalline NASICON was observed after heating the powder at 800 °C. In the XRD pattern of the precursor heated to 900 °C for 2 h (Figure 6), the NASICON phase is accompanied only by a small peak of tetragonal zirconia, demonstrating that the higher homogeneity and reactivity observed in solution is reflected by an improvement of the quality of the material with respect to our previous work.[9,11] However, the XRD pattern of the powder heated to 600 °C did not show the presence of NASICON, still amorphous, but tetragonal zirconia peaks were identified. The presence of zirconia is not then due to phase separation at high temperatures[3] but probably to hydrolysis of a small amount of the highly reactive Zr(O*t*-Bu)$_4$ before reaction with the other precursors. Studies are in progress involving less-reactive zirconium precursors to further improve the quality of the produced NASICON phase and to investigate the transport properties and sintering behavior of NASICON obtained by nonhydrolytic processes.

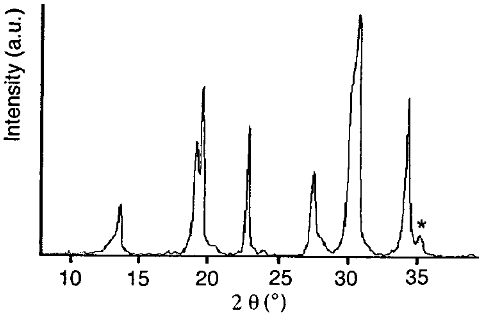

Figure 6. XRD pattern of NASICON precursor heated to 900 °C. An asterisk marks the only peak due to zirconia (ICDD no. 27-0997). All other reflections are due to NASICON (ICDD no. 35-412).

Conclusions

This study has shown that the nonhydrolytic sol–gel route can be a very convenient method for the preparation of a complex heterometallic oxide such as NASICON. The synthesis developed improved the homogeneity of the precursors and avoided the separation of unreacted zirconia or the long reaction time involved in previously studied hydrolytic sol–gel preparations. Homogeneity and complete reactivity in solution can be evidentiated by means of routine spectroscopic methods. The use of NMR spectroscopy in solution allows in fact step-by-step monitoring of the progress of the reaction, and such a technique appears to be a reliable method to predict the quality of the final material.

The information thus gained allows design of the optimal synthetic strategy, the value of which does reflect in the final material characteristic.

Acknowledgment. We thank Ms. C. D'Ottavi for her technical assistance, Mr. G. D'Arcangelo for recording the MS, and Dr. C. Bartuli (University of Rome "La Sapienza") for XRD measurements. This work was funded by MURST and CNR (PF MSTA II).

CM001128I