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The synthesis of NaSICON-type $ZrNb(PO_4)_3$ structure by the use of Pechini method

F. Ejehi[a], S.P.H. Marashi[a,*], M.R. Ghaani[b], D.F. Haghshenas[a]

[a]Department of Mining and Metallurgical Engineering, Amirkabir University of Technology, Hafez Ave., Tehran, Iran
[b]Dipartimento di Scienza Dei Materiali, Universit di Milano Bicocca, via R. Cozzi 53, 20125 Milano, Italy

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Abstract

Sol–gel routes for synthesizing super ionic conducting solids (e.g. NaSICON) are more economically advantageous and results in higher homogeneity and purity as well as finer grain size of the final product compared to other techniques. One prerequisite towards arriving at an effective sol–gel process is to cope with the obstacles at each step of solution and gel preparations, and heat treatment process. In the present work we attempt to develop a procedure for synthesis NaSICON-type $ZrNb(PO_4)_3$ based on the Pechini method, which offers easier process and better quality of the final product. Fourier Transform Infrared Spectroscopy (FTIR) was employed to evaluate the bonding characteristics of the obtained gel. The effect of heat treatment procedure on the purity and crystallographic structure of the final product was studied by the use of X-ray diffraction. Thermogravimetric Analysis (TGA) together with Differential Thermal Analysis (DTA) was used to investigate the variations of dried gel properties with temperature and to identify the appropriate heating process.

Keywords: A. Sol–gel processes; B. Electron microscopy; B. X-ray methods; C. Ionic conductivity

1. Introduction

Fast ion conductors are ionic conducting solid electrolytes with high conductivity below their melting point [1], which are extensively used in rechargeable batteries, fuel cells, chemical sensors and ion separators. In solid electrolytes, the conducting species are usually monovalent [2] or divalent [3] ions. The main problem of migration of higher valence ions stems from the strong electrostatic interaction between mobile cations and anions in the structure. However, in rhombohedral NaSICON (Na^+ Super Ionic CONductor) structure, which consists of a three-dimensional rigid framework with MO_6 octahedra and PO_4 tetrahedra sharing common corners [4], the mobile ion has sufficient space to move through the interstitial tunnels in surrounding anions.

In NaSICON structure with the general formula of $AM(PO_4)_3$, the appropriate selection of atom M is prerequisite for attaining high conduction of mobile ions especially at higher valences. In the case of tetravalent Zr ion, M should be a penta- (or more) valent ion to provide enough electrostatic interaction with anions and to enhance the Zr^{4+} ion mobility. $ZrNb(PO_4)_3$ [5] and $ZrTa(PO_4)_3$ [6] were the first structures synthesized via solid state route. Thereafter, it was shown that a partial addition of W^{6+} [7] and Si^{4+} [8] in $ZrTa(PO_4)_3$ structure can improve its conduction. The methods used for developing these compounds were solid state and sol–gel.

On the other hand, higher homogeneity and purity, finer grain size of the final structure, lower cost and low heat-treatment temperatures can be accounted as the advantages of the sol–gel method compared to the solid state for synthesizing such structures [9]. Among different types of sol–gel routes, the Pechini method offers several advantages including very stable citrate/metal complexes, lower cost, homogeneous compositions, high purity, lack of sensitivity to the moisture and low heat-treatment temperatures.

There are pertinent factors in the Pechini method which may affect the purity and characteristics of the final product. At gel production step, metal ions/citric acid

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*Corresponding author. Tel./fax: +98 21 66405846.
E-mail address: pirmarashi@yahoo.co.uk (S.P.H. Marashi).

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molar ratio (M:CA), citric acid/ethylene glycol molar ratio (CA:EG), and pH should be controlled to prevent the precipitation of undesirable compounds and to ensure the completion of the esterification reaction. Heat treatment is the next important step, which can be held in one or more passes. During heat treatment, organic materials are removed and the desired structure is obtained. However, in some cases, one or more crystalline intermediate phases may be formed at lower temperatures, which transform to the final structure by heating at higher temperatures.

To the authors' best knowledge, there is no work reporting the use of the Pechini method for synthesizing $ZrNb(PO_4)_3$ structure; it is very likely that the final product, obtained via this method, has the minimum amounts of impurities compared to other synthesizing technique [6]. In the present work, a procedure is developed for synthesizing $ZrNb(PO_4)_3$ NaSICON structure based on the Pechini sol–gel method for the first time. The effect of single-pass and multiple-pass heat treatment at different temperatures are studied while the parameters of M:CA, CA:EG, and pH were held constant. Fourier transform infrared spectroscopy (FTIR) was employed to investigate the complexing and esterification processes, and thermal analysis was used to optimize the heating temperatures to improve the obtained structure.

2. Materials and methods

2.1. Reagents and solutions

For synthesizing $ZrNb(PO_4)_3$ the following precursors of analytical grade were used: $ZrOCl_2 \cdot 8H_2O$ (Sigma-Aldrich), $NbCl_5$ (Alfa Aesar), $NH_4H_2PO_4$ (Sigma-Aldrich), citric acid (Merck), ethylene glycol (Merck), NH_4OH (Merck), and H_2O_2 (Merck). The detailed synthesis procedure of $ZrNb(PO_4)_3$ is presented in Fig. 1. Niobium chloride solution was prepared by dissolving a given amount of $NbCl_5$ in the diluted ammonia. Then, citric acid (CA) and hydrogen peroxide were added into the solution and stirred at around 70 °C for 1 h. The obtained transparent niobium solution was mixed with the aqueous solution of $NH_4H_2PO_4$ (phosphate solution). For the preparation of zirconium solution, CA was first dissolved in distilled water and then $ZrOCl_2 \cdot 8H_2O$ was introduced to this solution. By mixing the obtained solution with the phosphate solution (containing Nb^{5+} and PO_4^{3+}), ethylene glycol (EG) was added with molar ratio CA:EG of 1:2.

2.2. Experimental procedure

The final solution was heated at 96 °C to obtain a gel which then dried at 150 °C for 5 h. Two types of heat treatment; single-pass and multiple-pass heat treatment were applied on the dried gel. Many of NaSICON materials crystallize at temperatures up to 700 °C. However, for Zr/Hf NaSICON, this was not the case [7–15].

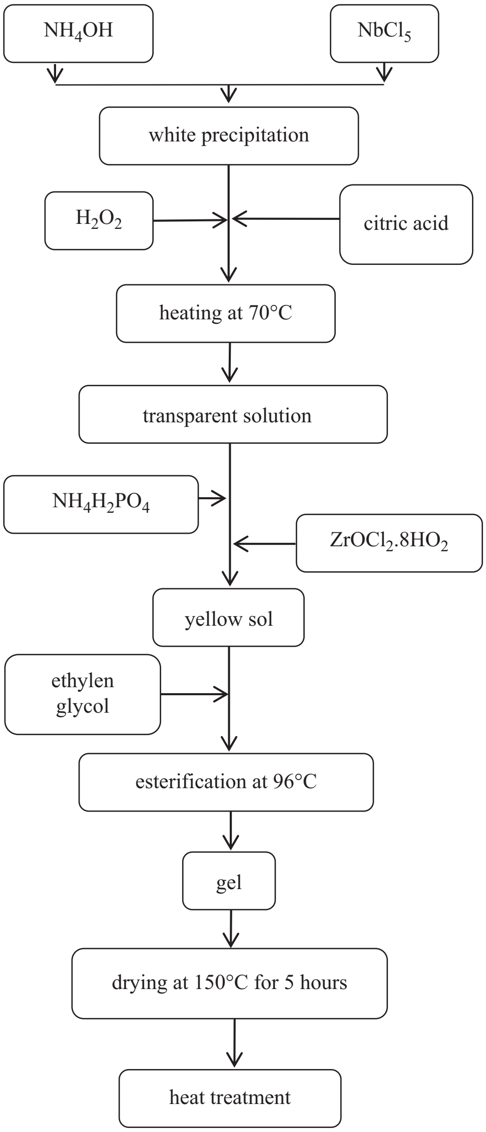

Fig. 1. Proposed flowchart for synthesis of $ZrNb(PO_4)_3$ based on the Pechini sol–gel method.

Therefore, in order to achieve a crystalline structure, it was decided to increase the calcination temperature to higher temperatures up to the capacity of the furnace used in this study. Thus, to find the suitable calcination temperature, the single-pass heat treatments were performed for 12 h at different temperatures of 700, 1000, and 1200 °C. The latter was reheated at 1200 °C for 12 h.

Based on our preliminary studies (unpublished data) and also the Bakar et al. (2010) [10] work on $BaZr_{0.85}Zn_{0.05}Y_{0.1}O_{2.95}$ the multiple-pass heat treatment procedure was performed at 3 stages of 400, 900, and 1200 °C for 12 h at each stage. Another multiple-pass heat treatment was applied on the dried gel at 300, 950, and 1300 °C for 12 h at each step. These temperatures were chosen based on the obtained thermal analysis data, which showed that a considerable weight loss occurred at these temperatures. Twelve hours retention time was implemented at each step to allow enough time for the reactions to get completed and for the volatile components to escape.

2.3. Analysis and characterization

IR spectrum of the dried gel was recorded using a Nicolet Nexus 870 FTIR spectrometer in the range of 400–4000 cm^{-1}. X-ray powder diffraction (XRD) patterns were obtained at room temperature using Cu-Kα radiation (Equinox 3000, Inel, France). The 2θ range in XRD analysis was 10–40° with a step size of 0.031°. PANalytical X'Pert HighScore software was used to interpret the XRD data. Simultaneous thermal analysis (STA) including thermogravimetric and differential thermal analyses (TGA–DTA) was performed on the dried gel by a NETZSCH STA 409 PC/PG instrument. The temperature range was 25–1460 °C with a heating rate of 10 °C min^{-1} using Al_2O_3 crucibles in air. The microstructures of the obtained powders heated at 1200–1200 °C, 400–900–1200 °C and 300–950–1300 °C were evaluated by a Philips XL36 scanning electron microscope.

3. Results and discussion

3.1. Preparation of sol and gel

Regarding the high affinity of Nb to form insoluble compounds in the aqueous solutions (especially Nb_2O_5), the stabilization of Nb solutions is the crucial step in the preparation of sol. For complete conversion of $NbCl_5$ to Nb_2O_5, NH_4OH was added into the system. By the addition of citric acid to the system (with the molar ratio of $NbCl_5$/CA=2.5) and in the presence of hydrogen peroxide, Nb_2O_5 precipitates were converted to dissolved species of Nb.

The mentioned Nb, phosphate and Zr solutions were mixed to obtain a solution containing soluble complexes of Nb, phosphate and Zr (sol). The mixing step of these two solutions strongly affects the stability of ion complexes and the transparency of the sol. Such effect is ascribed to the variation of pH during each step, which can cause the formation of an undesirable compound. Finally, by introducing EG to the sol and heating the system at 96 °C, a relatively transparent gel was obtained. The obtained gel was then dried at 150 °C for 5 h.

3.2. Characterization of the gel

Fourier Transform Infrared Spectroscopy (FTIR) is one of the analytical techniques available for studying a reactive system. In order to shed more light on the bonding characteristics of the dried gel, FTIR spectrum was employed (Fig. 2).

The peak that appeared at around 3415 cm^{-1} corresponds to the stretching of the O–H bonds in the citric acid derivatives and the trapped water molecules [16]. Moreover, the broad peak observed at 3165 cm^{-1} and the peak at 1721 cm^{-1}are assigned to the N–H stretching in ammonium group and the monodentate ligand of metal ion with carbonyl groups (COO−), respectively. The appearance of these peaks confirms both the presence of ammonium salts (in the forms of ammonium chloride and ammonium citrate) [17] and the occurrence of the complexing reaction [18]. Moreover, the bands at 1652 and 1385 cm^{-1} (which is slightly overlapped by the band at 1404 cm^{-1}) are allocated to the asymmetric and symmetric stretching mode of a carboxylate group, respectively; which can be considered as an evidence for the formation of CA complexes with both Nb and Zr [19]. The sharp peak that appeared at 1404 cm^{-1} is attributed to N–H bending of NH_4^+ in ammonium compounds [20].

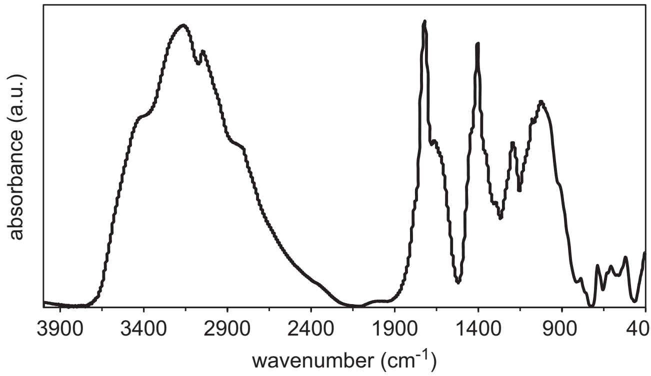

Fig. 2. FTIR spectrum of the gel prepared at 96 °C and dried at 150 °C for 5 h.

Additionally, esterification reaction between ethylene glycol and citric acid might be corroborated by C–O stretching band at 1194 and 1080 cm^{-1} [21]. The sharp peaks at 1024 cm^{-1} are related to P–O stretching modes [22] and the bands at 800 and 687 cm^{-1} are corresponded to Nb–O stretching and Nb–O–Nb bridging modes in polymeric intermediates, respectively [23]. Finally, the peaks observed at 595 and 520 cm^{-1} are ascribed to Zr–O and Zr–O–Zr bonds, respectively [24].

3.3. Heat treatment

The obtained dried gel contains the main species of NaSICON structure (i.e. zirconium, niobium, and phosphate ions) together with many undesired compounds such as organic materials and ammonium compounds. Thus, heat treatment of this gel is essential not only for removing the extra undesired species, but also for crystallization of NaSICON structure. Therefore, two heat treatment procedures, namely single-pass and multiple-pass, were applied.

The single-pass procedure was conducted at three different temperatures (700, 1000, and 1200 °C) for 12 h. Fig. 3 shows the XRD patterns of the heat-treated samples at different temperatures. According to the XRD pattern presented in Fig. 3(a), the single-pass treatment at 700 °C is an unsuccessful process for achieving a completely crystalline structure. Similar result was obtained for

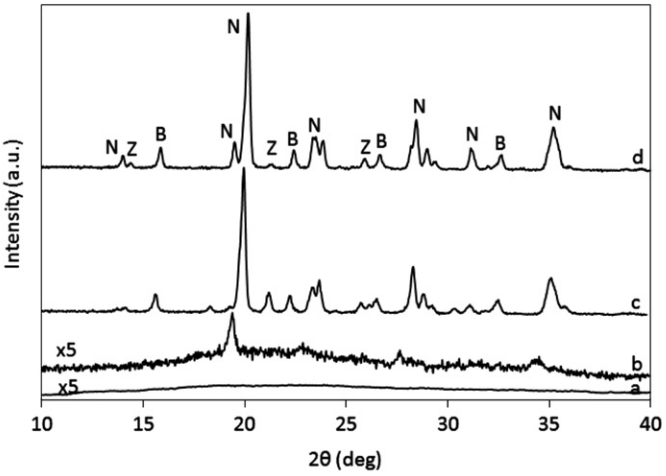

Fig. 3. XRD pattern of single-pass heated gel for 12 h at (a) 700 °C, (b) 1000 °C, (c) 1200 °C, and (d) 1200 °C (twice), (N = NaSICON, B = $NbPO_5$, Z = ZrP_2O_7).

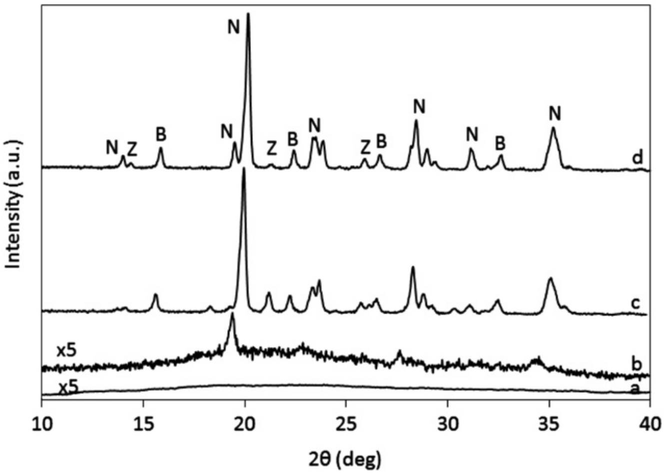

Fig. 4. XRD pattern of heated gel at 400, 900, and 1200 °C for 12 h. The impurity peaks are marked.

single-pass treatment at 1000 °C (Fig. 3b), except that a semi-crystalline phase was formed instead of completely amorphous structure.

Close observation of Fig. 3b reveals the appearance of a peak at 19.4° which is the main peak of NaSICON structure. Consequently, it was decided to conduct the single-pass heat treatment at a higher temperature (1200 °C). The XRD pattern corresponding to this procedure is presented in Fig. 3c in which the main peaks of NaSICON structure appear. Additionally, since there are still some additional peaks in the XRD pattern (Fig. 3c), which probably belong to unwanted niobium and zirconium phosphates, heat treatment was repeated at 1200 °C for 12 h. The resulted XRD pattern (Fig. 3d) shows the removal of some impurities and consequently higher purity as well as improvement of NaSICON-phase crystallinity (sharper 14° and 19.5° peaks).

In multiple-pass heat treatment, an initial two-step treatment was carried out at 400 and 900 °C and then it continued by a step at 1200 °C. The period of treatment in all steps was 12 h. The XRD pattern corresponding to this heat treated sample (Fig. 4) implies a NaSICON phase with the sharp and distinctive peaks. This pattern is in complete agreement with the pattern obtained by Imanaka et al. [6]. These findings indicate that multiple-pass heat treatment result in a better NaSICON structure (higher purity). However, in order to cope with the small amounts of impurities present in the final product, thermal analysis was employed for identification of the suitable heat treatment temperature.

3.4. *Simultaneous thermal analysis*

Based on the results discussed in Section 3.3, simultaneous thermal analysis was employed to investigate the detailed variations of dried gel properties with temperature. Fig. 5 illustrates the results of simultaneous thermal analysis (STA) of the dried gel. The first weight loss at 25–210 °C range observed on thermogravimetry (TGA) diagram is due to the elimination of the water molecules which are trapped in the polymer chains of the dried gel [25]. The second weight drop at 210–930 °C is related to the deformation of the polymer network, burnout of most of the organic residues, [26] and evaporation of ammonium compounds [20]. Finally, the third weight decrease at 930–1367 °C can be attributed to the evaporation of the residual carbon from the decomposed organic compounds generated in the previous stage [27].

These results also confirmed by differential thermal analysis (DTA) curve. The endothermic peaks observed at 235 and 307 °C can be due to the decomposition of CA and EG in the polymeric network [28]. The broad exothermic peak at around 850 °C may be due to the elimination of organic materials and the formation of a crystalline phase, which continues to an endothermic peak at 993 °C and another broad exothermic peak at around 1200 °C. Thus, it can be concluded that the crystalline phase forming at 900 °C is an intermediate phase and it converts to the final NaSICON structure at higher temperatures. This type of evolution was also reported by Sudreau et al. for $LiZr_2(PO_4)_3$ NaSICON-type structure [29]. Eventually, the endothermic peak at 993 °C may relate to the decomposition of remaining carbonates [27].

Based on the above findings, a multiple-pass heat treatment at 300, 950, and 1300 °C (the temperatures at which a considerable weight loss occurred) for 12 h was implemented. Fig. 6a shows the XRD pattern of the powder obtained from heating at 300 and 950 °C. The obtained structure is very similar to that obtained by single-pass heat treatment at 1200 °C. The crystalline structure indicates that employing a two-step heat treatment leads to a decrease in the temperature at which the amorphous phase disappears. This crystalline structure should be the intermediate phase produced before 993 °C. After heating up to 1300 °C, the NaSICON structure is completely formed with lower amounts of impurities (Fig. 6b). More comprehensive work is planned for thermodynamic and kinetic investigation of the phase formation.

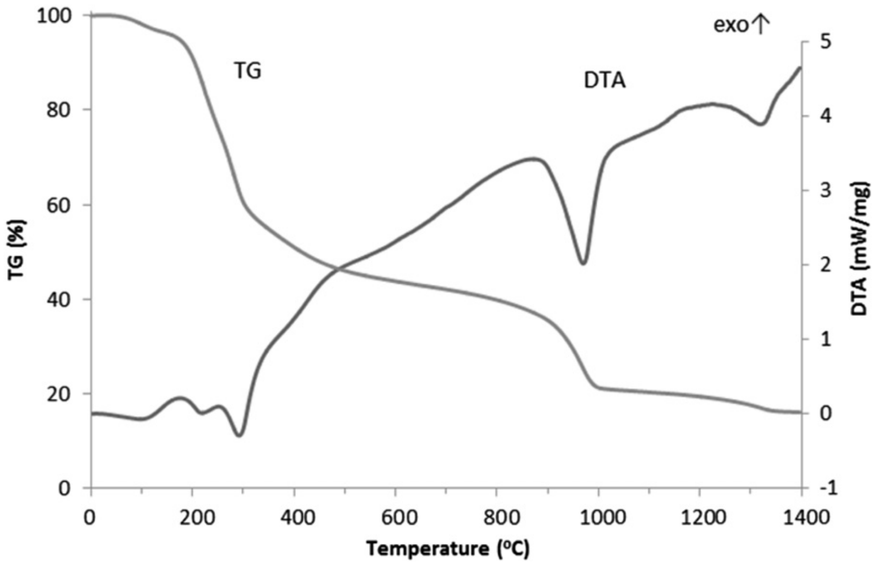

Fig. 5. The STA curves of the gel prepared at 96 °C and dried at 150 °C for 5 h.

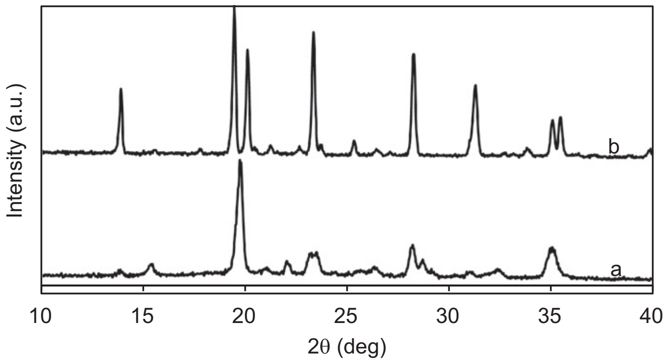

Fig. 6. XRD pattern of heated gel (a) at 300 and 950 °C for 12 h, and (b) after heating again at 1300 °C for 12 h.

3.5. Microstructure analysis

The SEM image of the powder heated at 1200–1200 °C (twice at 1200 °C) shows that the particle size is about 400 nm (Fig. 7a). It seems that the powder is partially sintered (non-spherical grains); however, the NaSICON peaks do not completely appear in the XRD pattern (Fig. 7a). The grain size of the powder heated at 400–900–1200 °C (Fig. 7b) is also around 400 nm; however, the shape of the grains is spherical. This results from the fact that the required time for breaking down the polymeric network and leaving the sample is provided by employing multiple-pass heat treatment at lower temperatures. In addition, reducing the residence time of the powder at high temperature (1200 °C) prevents the sintering and results in homogenous powders.

Fig. 7c shows the microstructure of the powder heat treated at 300–950–1300 °C. It is observed that the grains were sintered at this high temperature and some grain growth occurred. There are also some pores which are formed by evaporation of the remaining organic materials. Heating at 1300 °C reduces the sintering ability of the final powder compared to 1200 °C for further treatments, such as preparing a bulk; this means that the higher purity is obtained at the expense of sinterability which results in weaker ionic conductivity.

4. Conclusion

In this work, $ZrNb(PO_4)_3$ with NaSICON-type structure was successfully synthesized via the Pechini-type sol–gel method for the first time. The main findings in this study were the following.

In the preparation of appropriate solution (sol), Nb_2O_5 was effectively dissolved by the addition of citric acid in the presence of hydrogen peroxide. The precipitation problem was solved by changing the sequence of mixing the Zr, Nb and phosphate solutions. Eventually, ethylene glycol was added into the Nb–Zr sol and a relatively transparent gel was obtained by heating the system at 96 °C.

Fourier Transform Infrared Spectroscopy (FTIR) of the dried gel showed the characteristic peaks corresponding to the monodentate ligand of metallic ions with carbonyl groups (COO−) and C–O stretching, which confirmed the formation of CA complexes with both Nb and Zr and the occurrence of esterification reaction, respectively.

Based on the results obtained by Simultaneous Thermal Analysis (TGA – DTA), a multiple-pass heat treatment at 300, 950, and 1300 °C was implemented for 12 h. X-ray Diffraction pattern of the samples treated under this condition showed a NaSICON phase with the sharp and distinctive peaks which revealed fewer impurities compared to previously reported pattern.

SEM images of the powder obtained from a 400–900–1200 °C heat treatment process, in which its structure is the

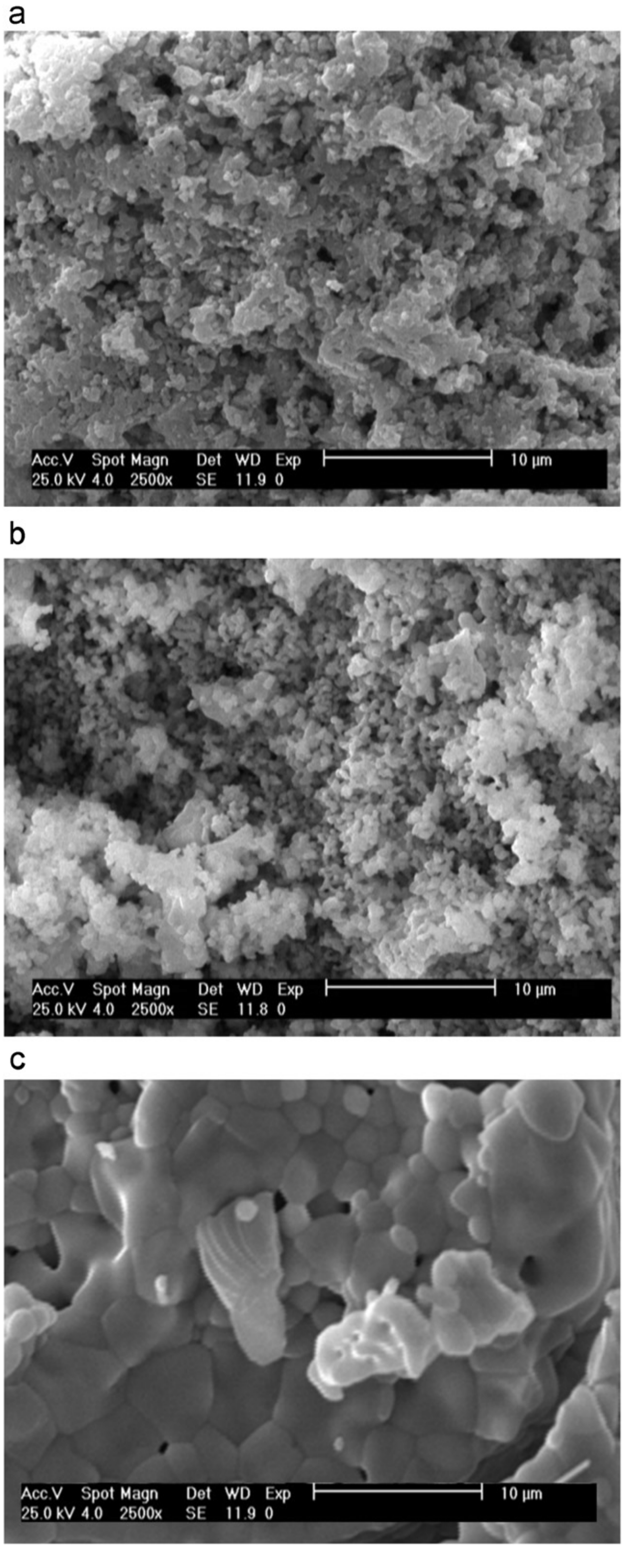

Fig. 7. SEM images of powders heated for 12 h at (a) 1200–1200 °C, (b) 400–900–1200 °C, and (c) 300–950–1300 °C.

same as the previously reported pattern, revealed the formation of spherical shaped grains with a size around 400 nm. It was found that the required time for breaking down the polymeric network and leaving the sample could be provided by employing multiple-pass heat treatment.

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