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Spark plasma versus conventional sintering in the electrical properties of Nasicon-type materials

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ABSTRACT

$Li_{1+x}M_xTi_{2-x}(PO_4)_3$ powders with x = 0 and 0.3 and M = Al, Cr and Fe have been sintered by conventional sintering (CS) and Spark Plasma Sintering (SPS), and the electrical properties have been compared. The use of SPS allows preparing samples with higher density at lower temperature and shorter time than the CS, avoiding segregation of secondary phases and with reduced crystallite size. The introduction of aluminum, chromium and iron in the $LiTi_2(PO_4)_3$ (LTP) clearly enhances ionic conductivity even if the samples have similar densities. Despite the different level of density reached with CS and SPS, the activation energies of dc and grain boundary contributions are very similar and the differences in ionic conductivity are determined by pre-exponential factors. The samples produced by SPS showed a well-defined grain boundary meaning a more homogenous electrical contact.

1. Introduction

Solid lithium conductors have been attracting a great interest during the last decades due to their potential applications in lithium batteries, sensors and fuel cells [1–9]. Nasicon-type materials were first discovered as three-dimensional ionic conductors and since then many studies have focused on the development of Nasicon materials with optimized properties. $LiTi_2(PO_4)_3$ (LTP) and its derivatives are among the best candidates [10–19]. As it has been repeatedly described, the electrical properties of LTP are highly improved by the substitution of Ti^{4+} with a trivalent metal giving rise to compounds of formula $Li_{1+x}M_xTi_{2-x}(PO_4)_3$ [10,20–22]. There are two reasons for the improvement of the ionic conductivity: the increase in the concentration of carriers (Li^+) and the enhanced density of the powders. In a previous work, we have demonstrated that the concentration of carriers is strongly affecting the ionic conductivity in the way that the displacement of ions from the M1 position to the M2′, gives rise to a higher disorder of ions within the structure [23]. However, apart from the composition, the ionic conductivity of Nasicon materials has also a strong dependence on their density [13,24]. Traditionally, two methods have been used to increase the density of materials: the cold sintering and the melting of the material with a subsequent quenching. As it has been proved, none of these methods succeeded in the fully densification of LTP phases [25,26]. Nasicon compounds are well known to be difficult to densify by the traditional techniques (conventional sintering or hot press) [27].

The Spark Plasma Sintering (SPS) is a pressure assisted sintering method consisting in the application of a pulsed DC current along with uniaxial pressure. SPS allows a faster densification than the conventional sintering methods at lower temperature, giving rise to higher density, smaller grain size, clearer grain boundaries as well as other attractive properties [28]. The critical temperature above which the grain growth rate becomes appreciable is largely determined by the properties of the powder precursors, e. g. their particle size, reactivity, degree of agglomeration, etc., but also by the applied heating rate and pressure [29]. In order to prepare dense samples with a very limited grain growth, it is necessary to map up the sintering parameters [30]. SPS is nowadays attracting the attention of many researches with the aim to obtain all-solid-state-batteries [31–34]. However, until now only a few papers reporting the SPS of Nasicon materials have been published [35]. $LiTi_2(PO_4)_3$ obtained by hydrothermal synthesis was sintered by SPS at 1200 °C, but only the 81% of the theoretical density was

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achieved [36]. Later on, the SPS of the same compound obtained by solid state reaction was reported and, on the same sintering conditions, the 95% of the theoretical density was achieved [37]. Al-substituted LTP has been sintered by SPS and fully dense materials were obtained [38–40]. Other Nasicon materials, such as $LiHf_2(PO_4)_3$ and $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$, have been successfully sintered using SPS [41,42]. Nevertheless, to the best of our knowledge, there is no paper reporting the systematically study of M^{3+}-substituted LTP materials sintered by SPS.

In this work, Spark Plasma Sintering has been used in order to obtain full dense pellets with composition $Li_{1+x}M_xTi_{2-x}(PO_4)_3$. The sintering parameters were optimized to obtain the highest density and avoid grain growth. Four different materials were densified: $LiTi_2(PO_4)_3$ (LTP), $Li_{1.3}Al_{0.3}Ti_{1.7}(PO_4)_3$ (LATP), $Li_{1.3}Cr_{0.3}Ti_{1.7}(PO_4)_3$ (LCTP) and $Li_{1.3}Fe_{0.3}Ti_{1.7}(PO_4)_3$ (LFTP). With the aim of studying the differences in the sintering behaviour of $LiTi_2(PO_4)_3$ when adding Al, Cr and Fe, the substitution degree in LTP was fixed. The electrical properties of the fully dense materials are compared with samples with low density produced by conventional sintering that were already reported by us [23], in order to determine the effect of the density on the ionic conductivity of these compounds.

2. Material and methods

2.1. Sample preparation

$Li_{1+x}M_xTi_{2-x}(PO_4)_3$ samples with x = 0, 0.3 and M = Al, Cr and Fe were prepared by the Pechini sol–gel method following the procedure reported elsewhere [43]. The obtained powders were then compressed and densified by conventional sintering (CS) and spark plasma sintering (SPS). CS treatment consisted on the cold pressing of the powder into pellets of 13 mm diameter and 1 mm thickness using a uniaxial pressure of 150 MPa and a subsequent sintering treatment at 1000 °C for 12 h. SPS experiments were carried out in an SPS unit Dr. Sinter 2050 (SPS Syntex Inc., Japan). Before SPS treatment, samples were mechanically milled in ethanol at 100 rpm during 10 min for homogenization. After drying, powders were loaded in a cylindrical graphite die with 12 mm of inner diameter and enclosed by graphite papers. In order to isolate the sample from the electrical current, powders of Al_2O_3 were placed both on the bottom and the top of the sample in a way that a nonconductive layer of 1.5 mm thickness was performed. The die was heated by allowing a pulsed direct current to pass through it with pulses of 3.3 ms and a pulse sequence of 12 pulses On: 2 pulses Off. The On–Off voltage creates spark discharge, generating high temperature and Joule heating between particles [44]. The maximum voltage and current were 3.5 V and 635 A respectively. The temperature was measured with a thermocouple inserted into the graphite die. The set-up is provided with a dilatometer for recording the shrinkage. Linear shrinkage, ΔL, temperature, pressure, average voltage and current are recorded during the process. The ΔL-values were corrected for the contribution related to the expansion of the graphite die set and the Al_2O_3 layers through a zero-curve. In a first set of experiments, the kinetic window within which it is possible to obtain dense ceramics and simultaneously reduce grain growth, were defined using standard conditions, meaning a constant heating rate of 50 °C/min and a pressure of 75 MPa. The onset temperature (T_0) is defined as the temperature at which shrinkage starts. The temperature at which ΔL is constant, that is, the sample has achieved its final density, is known as final temperature (T_f). During the experiments, the onset and final temperatures of densification were determined. When T_f was reached, the pressure was released and sample was cooled down. After sintering, SPS samples were polished to remove the graphite paper and annealed in air at 700 °C for few hours.

2.2. Characterization

The density of the samples was determined by the Archimedes method using water as the immersion fluid.

XRPD patterns were collected on a Philips X'Pert PRO instrument using CuKα_1 radiation,(45 kV, 40 mA) with a PW 3050/00 goniometer in a Bragg–Bretano configuration and a Germanium X′ Celerator detector. A step scan of 0.033° (2θ) in the range 10–120° and a counting time of 350 s were employed. Quantitative phase analysis was carried out by means of the Rietveld method implemented in the Fullprof software [45].

Microstructural studies were made by FEG–SEM observations of the fracture surface of the pellets using secondary electrons. A JEOL JSM 6335F microscope was used working at 40 kV accelerating voltage. The mean grain size has been obtained from the images measuring at least 100 grains.

The electrical properties were analyzed by impedance spectroscopy. Measurements were carried out in a BDS80 from Novocontrol, in the frequency range 10^{-2}–10^7 Hz at selected temperatures between −150 and 250 °C with the integrated Quatro temperature control system with accuracy of ±0.1 K. Electrical contacts were made with silver paint and an inert atmosphere was ensured by measuring the samples under N_2 flow.

3. Results

3.1. Densification by SPS

Table 1 shows the observed T_0, T_f and final density for each sample, together with the experimental parameters used in the standard experiments. Density values of samples processed by CS are also included for comparison.

As it can be observed, the SPS gives rise to high density pellets in a shorter time than the CS. Using both techniques, the highest values were reached in the LATP samples and the lowest in the LTP and LCTP. Values of at least 85% of the theoretical density were obtained using SPS in contrast with the poorly densified samples obtained by CS. Once activated, the densification occurs very fast, within less than 10 min, and in a very narrow temperature interval. The onset of shrinkage starts at 720–760 °C for the LPT, LATP and LCTP samples and at 540 °C for the LFTP. The onset of shrinkage is generally known as the starting point of the grain sliding mechanism, where the open pore channels start to shrink [46]. Fig. 1 shows the linear shrinkage rate plotted versus time observed during SPS. The linear shrinkage rate is defined as $d(-\Delta L/L_o)/dt$, with L_o being the thickness of the green body at room temperature under

Table 1
Sintering parameters of standard experiments, T_0, T_f and final density values. The values of density of samples obtained by CS is added for comparison.

Sample	Heating rate	T_0	T_f	Holding time	Pressure	Density SPS	Density CS
LTP	50 °C/min	760 °C	950 °C	5 min	75 Mpa	90%	60%
LATP	50 °C/min	760 °C	950 °C	3 min	75 Mpa	98%	71%
LCTP	50 °C/min	720 °C	850 °C	5 min	75 Mpa	86%	51%
LFTP	50 °C/min	540 °C	700 °C	0 min	75 Mpa	95%	65%