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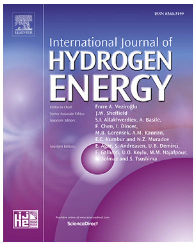

Effect of Sr^{2+} doping on sintering behavior, microstructural development and electrical properties of $LaPO_4 \cdot nH_2O$ nanorods prepared by dry mechanical milling

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ABSTRACT

The effect of Sr^{2+} doping on the presence of second phases, sintering behavior, microstructural development, and electrical properties of $LaPO_4 \cdot nH_2O$ nanorods ($La_{1-x}Sr_xPO_{4-x/2}$ where $x = 0.025$ and 0.05) obtained by a dry mechanochemical milling process was investigated. When Sr^{2+} is present monazite-type $La_{1-x}Sr_xPO_4$ nanopowders were obtained instead of rhabdophane-type $LaPO_4 \cdot nH_2O$. In addition, Sr^{2+} doping implies a larger P/La ratio and it enhances the formation of lanthanum tryoxophosphate ($La(PO_3)_3$), a thermodinamically stable phase, in doped samples. Dilatometric studies reveal a shift of the maximum shrinkage rate at lower temperatures for doped samples, with larger shifts with higher Sr^{2+} contents. This shift is related to the presence of oxygen vacancies but also to a higher content of $La(PO_3)_3$. Furthermore, the derivative of the linear shrinkage curves for all the samples showed peaks at temperatures higher than 1300 °C that are associated to the volatilization of P_4O_{10} gas and to the recrystallization of monazite from the incongruent melting of $La(PO_3)_3$. After the dilatometric tests at 1500 °C the samples showed polygonal grains with a bimodal size distribution. For the doped samples the smaller grains do not present Sr^{2+} in their composition and it is related to those grains form from the recrystallization of monazite-$LaPO_4$ formed in turn from $La(PO_3)_3$. The total conductivity of the studied samples ($x = 0.05$) is higher for the samples sintered at 1000 °C for 1 h than for those sintered at 1500 °C without any dwell time. It can be due in part to the fact that the smaller grains of the samples sintered at 1500 °C do not contain Sr^{2+} and it can hinder the charge transport.

Introduction

Lanthanum orthophosphate doped with acceptors such as Sr^{2+} is a proton conductor at high temperature [1–7]. The concentration of protonic defects in the material depends on dopant content. However, a homogeneous distribution of the dopant is also very important for attaining adequate proton conductivity values. Lanthanum orthophosphate is normally prepared by chemical precipitation methods using $La(NO_3)_3$,

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$LaCl_3$, $La(NO_3)_3{\cdot}6H_2O$, La_2O_3 or $La(OH)_3$ as lanthanum agents and H_3PO_4 or $(NH_4)_2HPO_4$ as phosphating agents [8–12]. However, these methods are time-consuming and require multiple step reactions, precise pH control or lead to harmful by-products such as hydrochloric acid [8,10,11]. In this study, dry mechanical milling has been used to obtain Sr^{2+}-doped $LaPO_4$ nanoparticles. This method provides a direct, simple, economical and low-temperature route free of solvents to obtain, eventually, any ceramic of interest [13]. In addition, the knowledge of the behavior of Sr^{2+}-doped $LaPO_4$ as a function of the temperature (i.e., dilatometric and sintering and microstructural development studies) is an area of interest in materials science since the use of this type of materials as electrolyte requires homogeneous and dense materials free of second phases. However, that behavior is unknown for powders prepared by dry mechanochemical milling. On the contrary, the sintering behavior of undoped $LaPO_4{\cdot}nH_2O$ prepared by both wet chemical and dry mechanochemical milling routes has been previously reported although the phosphate precursor was different than that used in this study in the mechanochemical milling process [14,15]. It has been demonstrated that the presence of $La(PO_3)_3$ as second phase in the $LaPO_4{\cdot}nH_2O$ powders has two opposite consequences during sintering: it decreases sintering temperature but it also promotes fast grain growth. This leads to the formation of coarse grains with a high amount of intragranular pores that cannot be resorbed [15]. Consequently, due to its detrimental influence on sintering process, more particularly on the microstructural design of sintered ceramics, $La(PO_3)_3$ must be eliminated or at least minimized. However, $La(PO_3)_3$ is thermodynamically stable according to the La_2O_3-P_2O_5 phase diagrams [16–18]; for its removal Bregiroux et al. [15] proposed to heat the raw powders of $LaPO_4$ at 1400 °C for 1 h. However, such process can provoke the formation of hard agglomerates that hinder the sintering process and can enhance the formation of second phases. Furthermore, the presence of second phases containing Sr^{2+} or not has deleterious effects on the proton conductivity of these materials.

Then, this paper is devoted to study the effect of Sr^{2+} on the structure of $LaPO_4{\cdot}nH_2O$, on the presence of second phases, on the sintering behavior, and on the microstructural development of $LaPO_4{\cdot}nH_2O$ nanorods prepared by a dry mechanical milling route. The electrical properties of samples doped with $x = 0.05$ were also measured under different atmospheres. To the best of my knowledge, those studies have not been previously reported in samples prepared by dry mechanical milling. To this end, XRD, IR, Raman, DTA-TG, FEG-SEM, HREM, dilatometric, and four-probe dc conductivity studies have been performed.

Experimental procedure

Powder synthesis

Powders of nominal composition $La_{1-x}Sr_xPO_{4-x/2}$ ($x = 0$, 0.025, and 0.05, i.e., $LaPO_4$, $La_{0.975}Sr_{0.025}PO_{3.988}$ and $La_{0.950}Sr_{0.050}PO_{3.975}$) were prepared by a mechanically activated chemical reaction starting from $La(NO_3)_3{\cdot}6H_2O$ (Sigma-Aldrich Inc., 99.99%), $Sr(NO_3)_2$ (Sigma-Aldrich Inc., 99.9%), and $(NH_4)_2HPO_4$ (Sigma-Aldrich Inc., 98%). Reagents were weighed out as required by stoichiometry and placed in 125 ml zirconia containers together with six 20 mm diameter zirconia balls (mass ≈ 24 g) as to keep the balls-to-powder mass ratio equal to 10:1, as described elsewhere [19]. In a typical experiment, a 15 g batch of reactants was dry milled in air for 3 h in a planetary ball mill (Pulverisette 6, Fritsch, Germany) by using a rotating disc speed of 350 rpm with reversed rotation every 20 min. Milled powders were repeatedly washed with deionized water to eliminate NH_4NO_3 formed as by-product, and dried at 120 °C for 4 h [19].

Characterization techniques

XRD, IR, and Raman studies

Resulting powders were analyzed by X-ray powder diffraction in a Siemens D-5000 (Germany) using Ni-filtered CuK_α radiation ($\lambda = 1.5418$ Å) from 10 to 60-70° at a step scan rate of 2°/s collected at room temperature. In addition, in order to establish the presence of $La(PO_3)_3$ good resolution XRD patterns were obtained using a low step size (0.02°) and a counting time of 10 s.

As-prepared powders and calcined powders after drying were also characterized by Infrared Spectroscopy (IR) in a Perkin Elmer IR 1760X spectrometer (MA, USA) using KBr pellets.

Raman spectra were recorded on a Renishaw spectrometer (In Via, UK) with an excitation wavelength of 514 nm produced by Ar^+ laser. The 200-3200 cm^{-1} spectral range was evaluated using 10 scans for each measurement. The samples were focused with a Leica optical microscope with a 50× magnification objective lens. A sharp line of silicon at 520 cm^{-1} was taken as a reference in the Raman shift scale.

DTA-TG studies

Differential thermal analysis and thermogravimetry (DTA-TG) of the as-synthesized powders was performed in dried air in a Perkin Elmer, Model DTA7, and Model TGA7 analyze (MA, USA), respectively, using a typical sample size of 10 mg in a Pt crucible and a heating rate of 5 °C/min up to 1400 °C.

FEG-SEM-XEDS, TEM-XEDS, and HREM-XEDS characterization

As-prepared powders were characterized by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were carried out on a Jeol 2000FX (Tokyo, Japan) microscope working at 200 keV, equipped with an ISIS analyzer system that characterized the local composition by X-ray energy-dispersive spectrometry (XEDS). Finally, HREM-SAED-XEDS analyses were performed using a field-emission gun microscope (JEOL JEM-2011, Tokyo, Japan), operated at 200 keV accelerating voltage, equipped with an ISIS analyzer system that characterized the local composition by XEDS. The image processing was done using the ImageJ 1.45 software (Wayne Rasband, NIH, Bethesda, Maryland, USA), utilizing the standard diffraction lines of hexagonal $LaPO_4{\cdot}0.5H_2O$ (PDF card 00-046-1439), monoclinic $LaPO_4$ (PDF card 01-083-0651) and $La(PO_3)_3$ (PDF card 033-0717) for the interpretation of the XRD patterns and HREM images. All this microscopy effort was

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