Effect of Sr^{2+} Doping on Sintering Behavior, Microstructural Development and Electrical Properties of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ 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 $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ nanorods ($\text{La}_{1-x}\text{Sr}_x\text{PO}_{4-x/2}$ where $x = 0.025$ and 0.05) obtained by a dry mechanochemical milling process was investigated. When Sr^{2+} is present monazite-type $\text{La}_{1-x}\text{Sr}_x\text{PO}_4$ nanopowders were obtained instead of rhabdophane-type $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$. In addition, Sr^{2+} doping implies a larger P/La ratio and it enhances the formation of lanthanum tryoxophosphate ($\text{La}(\text{PO}_3)_3$) 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 $\text{La}(\text{PO}_3)_3$. 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 $\text{La}(\text{PO}_3)_3$. 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 in their composition and it is related to those grains form from the recrystallization of monazite- LaPO_4 formed from $\text{La}(\text{PO}_3)_3$. 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.

Keywords: Mechanochemical processing, Sintering, Electron microscopy, $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$, Sr^{2+} -doped LaPO_4 , $\text{La}(\text{PO}_3)_3$

1. 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 $\text{La}(\text{NO}_3)_3$, LaCl_3 , $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, La_2O_3 or $\text{La}(\text{OH})_3$ as lanthanum agents and H_3PO_4 or $(\text{NH}_4)_2\text{HPO}_4$ 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 $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ prepared by both wet chemical route 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 $\text{La}(\text{PO}_3)_3$ as second phase in the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ 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, $\text{La}(\text{PO}_3)_3$ must be eliminated or at least minimized. However, $\text{La}(\text{PO}_3)_3$ 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 1h. However, such process can provoke the formation of hard agglomerates that hinder the sintering process. 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 $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$, on the presence of second phases, on the sintering behavior, and on the microstructural development of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ 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.

2. Experimental Procedure

2.1. Powder synthesis

Powders of nominal composition $\text{La}_{1-x}\text{Sr}_x\text{PO}_{4-x/2}$ ($x = 0, 0.025$, and 0.05 , i.e., LaPO_4 , $\text{La}_{0.975}\text{Sr}_{0.025}\text{PO}_{3.988}$ and $\text{La}_{0.950}\text{Sr}_{0.050}\text{PO}_{3.975}$) were prepared by a mechanically activated chemical reaction starting from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Sigma-Aldrich Inc. 99.99%), $\text{Sr}(\text{NO}_3)_2$ (Sigma-Aldrich Inc. 99.9%), and $(\text{NH}_4)_2\text{HPO}_4$ (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. In a typical experiment, a 15 g batch of reactants was dry milled in air for 3 h in a planetary ball mill 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 hours [19].

2.2. Characterization techniques

2.2.1. XRD, IR, and Raman studies

Resulting powders were analyzed by X-ray powder diffraction in a Siemens D-5000 using Ni-filtered CuK_α radiation ($\lambda = 1.5418 \text{ \AA}$) from 10 to $60\text{-}70^\circ$ at a step scan rate of $2^\circ/\text{s}$ collected at room temperature. In addition, in order to establish the presence of $\text{La}(\text{PO}_3)_3$ 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 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 50x magnification objective lens. A sharp line of silicon at 520 cm⁻¹ was taken as a reference in the Raman shift scale.

2.2.2. 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 analyser, 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.

2.2.3. 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 LaPO₄·0.5H₂O (PDF card 00-046-1439), monoclinic LaPO₄ (PDF card 01-083-0651) and La(PO₃)₃ (PDF card 033-0717) for the interpretation of the HREM images. All this microscopy effort was aimed at determining morphological features of the undoped LaPO₄·*n*H₂O and Sr²⁺-doped LaPO₄ powder particles both in their as-synthesized condition and after the calcination at 800 °C for 12 h in air.

The microstructure of the sintered samples was analyzed on fresh fractures by means of Field-emission scanning electron microscopy-energy dispersive x-ray (FEG-

SEM-XEDS) (Hitachi S-4700 type I, Tokyo, Japan). Microstructures of fresh-fracture surfaces of the samples after the dilatometric essays were also analyzed with the same microscope.

2.2.4. Dilatometric and sintering studies

Dilatometric tests were carried out at heating and cooling rates of 5°C/min from room temperature and up to 1500°C in air without any dwell time. They were performed in a differential dilatometer with alumina rod (Adamel Lhomargy, DI24, Brie France), on uniaxially and isostatically pressed (200 MPa) discs 2-3 mm thick and 6 mm in diameter. In addition, samples were also sintered in air at 1000°C for 1 h (heating and cooling rates of 5°C/min).

2.2.5. Electrical characterization

Four-probe dc conductivity measurements were applied to determine the total conductivity of the sintered samples under dry and wet atmosphere in the temperature range of 350-1000°C. Platinum was used as electrodes. Each curve was obtained after equilibration at 1000°C for 1 h and was recorded during ramps of decreasing temperature of 0.5°C/min. The samples were put in a closed high-temperature conductivity chamber. The atmosphere was flowing dry air or air wetted by bubbling through H₂O and subsequently through a saturated solution of KBr in H₂O at room temperature to obtain a constant relative humidity around 80% to avoid condensation.

3. Results and discussion

3.1. Powder synthesis and XRD, IR, and Raman studies

In this work, a solid state metathesis and highly exothermic reaction between reactants is produced by dry mechanical milling. Thus, nitrate and phosphate anions exchange cations on milling the initial mixture as follows:

yielding a mixture of (La,Sr)PO₄ and NH₄NO₃ and thus, providing an easy route to synthesize the target phase without the need of a furnace while considerably reducing the time reportedly needed to obtain the same product by using different processing methods such as chemical reactions in an aqueous solution [7-11]. NH₄NO₃ is easily removed by washing with water. Furthermore, the final particle size of (La,Sr)PO₄ is also reduced as compared to other milling methods.

Despite of the milling step being carried out without added water (“dry milling”), the product obtained when the process is performed in the absence of Sr(NO₃)₂, i.e. by mixing hydrated lanthanum nitrate and ammonium hydrogenphosphate, is rhabdophane-type LaPO₄·*n*H₂O (hexagonal, space group *P*6₂22; PDF 46-1439) (Fig. 1a) instead of monazite. This result suggests an important role in the synthesis procedure for the water molecules included in the hydrated salt used as the lanthanum source. Thus, the synthesis of the Sr²⁺-doped lanthanum phosphates will probably involve the initial formation of rhabdophane with further milling and the presence of strontium atoms promoting its in-situ transformation to monazite (monoclinic, space group *P*2₁/*n*; PDF 43-1326) which is the product finally identified by XRD after the washing step (Fig. 1b). Despite of this, water molecules are intentionally omitted from equation described above because of the complexity of balancing the process in a milling scenario where characterizing intermediates is very difficult. During the mechanical activation of powder mixtures, particles trapped at the contact point between colliding balls are simultaneously and almost instantaneously subjected to very high pressures and temperatures. Thus, dehydration processes are common during mechanical milling and some authors have reportedly achieved the partial dehydration of weinschenkite REPO₄·2H₂O (RE = Dy, Y, and Er) and thus, its phase transformation to rhabdophane REPO₄·*n*H₂O (*n* = 0.7-0.8), by prolonged milling in alumina vials [20,21].

Fig. 1. XRD patterns of (a) $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and (b) Sr^{2+} -doped LaPO_4 ($x = 0.05$) prepared by dry mechanical milling after washing and drying.

Fig. 1a) shows representative XRD patterns of $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ nanorods with rhabdophane-type crystal structure ($x = 0$) in its as-synthesized condition. Meanwhile $\text{La}_{1-x}\text{Sr}_x\text{PO}_4$ nanopowders have the monazite-type crystal structure when $x = 0.025$ and 0.05 in their as-synthesized condition (Fig. 1b). Then, when the synthesis is carried out in the presence of $\text{Sr}(\text{NO}_3)_2$ the product obtained is monazite LaPO_4 as unique phase and firing the first at temperatures $\sim 700^\circ\text{C}$ is needed in order to trigger the transition from rhabdophane to monazite (see DTA-TG section).

According to the literature, the site symmetry of tetrahedral PO_4^{3-} anions in the hexagonal hydrated $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ structure is C_2 , and therefore the fundamental vibrational modes allowed are only ν_1 , ν_3 , and ν_4 [22]. As can be seen in Fig. 2a), these three active vibrational modes are experimentally detected, thus confirming that the as-synthesized powders crystallize as rhabdophane phase for the undoped samples; specifically, ν_1 (that is, the P–O symmetric stretching) is located at 965 cm^{-1} , ν_3 (that is, the P–O asymmetric stretching) is located at 1057 cm^{-1} , and ν_4 (that is, the O–P–O asymmetric bending vibrations) are located at 546 , 576 , and 620 cm^{-1} .

For the doped samples (Fig. 2b), $x = 0.025$), the PO_4^{3-} site symmetry in the monoclinic (monazite) LaPO_4 structure corresponding to C_1 is observed [22]. Then, at low frequencies the nine characteristic bands resulting from the distortion of the tetrahedral phosphate groups in the nine-fold coordinated La atoms, can be observed (five bands in the ν_3 region): 1094, 1054, 1014, 993, and 953 cm^{-1} , and four bands as two doublets in the ν_4 region [23,24]. In this study and according to Hezel et al. [22] in the ν_4 region four bands appear as two doublets (539, 563, 577, and, 626 cm^{-1}); the upper double split about 45 cm^{-1} and the lower doublet by 24 cm^{-1} . In addition, the spectrum presents one very small band at 803 cm^{-1} which could be assigned to trioxophosphate groups (PO_3^-) related to $\text{La}(\text{PO}_3)_3$ [11,25,26]. It must be noted that, probably due to the very low intensity of PO_3 vibrations and to the presence of intense and broad vibration bands of PO_4 groups in the domain 990-1100 cm^{-1} , there was no evidence for the presence of a band near 1000 cm^{-1} mentioned also in the literature for cyclic trioxophosphate groups [11,25,26]. According to Gushikem et al. [27] the group $(\text{PO}_3)_3$ corresponds to a cyclic polytrioxophosphate and its vibrations were detected on the IR spectra for the powder calcined at 1000°C [27] with its characteristic bands at 770 and 1250 cm^{-1} (IR), which are the two most intense bands of vibrations of trioxophosphates, identified as $\nu_{\text{symmetric}}$ O-P-O and $\nu_{\text{asymmetric}}$, respectively. In this study, the band at 770 cm^{-1} is not observed meanwhile a band observed at 1262 cm^{-1} that can correspond to $\text{P}_2\text{O}_7^{4-}$ is observed [28]. The presence of $\text{P}_2\text{O}_7^{4-}$ band may be resulted from the presence of HPO_4^{2-} where the substitution of HPO_4^{2-} for PO_4^{3-} is possible. The weak intensity of the PO_3^- band at 803 cm^{-1} [26], that is also associated to the $(\text{PO}_3)_3$ groups, and the absence of the bands at 770 and at 1250 cm^{-1} do not allow to confirm the presence of $\text{La}(\text{PO}_3)_3$ in the as-prepared powders.

In Fig. 2c) the spectrum of the undoped lanthanum phosphate after calcination at 725°C for 1 min is shown. The presence of four bands as two doublets in the ν_4 region is characteristic of the vibrations of phosphate groups in the monoclinic structure of monazite-type LaPO_4 , as it is mentioned above [23-25]; in this case, these bands are found at 538 and 561, and 577 and 619 cm^{-1} , being the lower doublet splitting 23 cm^{-1} and the upper doublet 42 cm^{-1} . In addition, the five characteristic bands of the ν_3 region at 953, 995, 1017, 1060, and 1091 cm^{-1} can be clearly observed [23-25]. This result agrees well with that obtained by DTA-TG where an exothermic peak at 710°C is detected and it can be attributed to the rhabdophane-monazite transformation (see next

section). The resolution of the phosphate vibration bands in the domain $1100\text{-}990\text{ cm}^{-1}$ is low and it can be related with the low crystallinity of the monazite phase which is formed at 710°C , as it is mentioned above. These results are in agreement with those obtained by XRD.

The resolution of the phosphate vibration increases with the calcination temperatures as it is expected, indicating a higher crystallization of the monoclinic phase. As in the previous spectrum (Fig. 2b), the weak intensity of the PO_3^- band at 803 cm^{-1} , the absence of the band at 770 cm^{-1} together with the fact that the band at 1262 cm^{-1} can correspond to another phosphate group do not allow to confirm the presence of $\text{La}(\text{PO}_3)_3$ either in the as-prepared or in the calcined powders.

Fig. 2. IR spectra of samples just milled and dried (a) as-prepared $\text{La}_{1-x}\text{Sr}_x\text{PO}_{4-x/2} \cdot n\text{H}_2\text{O}$ where $x = 0$, (b) as-prepared $\text{La}_{1-x}\text{Sr}_x\text{PO}_{4-x/2}$ where $x = 0.025$ ($\text{La}_{0.975}\text{Sr}_{0.025}\text{PO}_{3.988}$), and (c) the undoped lanthanum phosphate after calcination at 725°C for 1 min.

The as-synthesized $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ compound crystallizes in the hexagonal space group $P6_222$, as it is mentioned above, and has three formulae per primitive cell (18 atoms) and therefore 54 normal modes. The Raman active ones are $3A_1 + 8E_1 + 10E_2$, while $5A_2 + 10E_1$ are the infrared active modes. P^{5+} and La^{3+} ions are located at high

symmetry sites (Wyckoff positions 3c and 3d, respectively) and participate only in Raman modes $1E_1+2E_2$. Therefore, the majority of the observed bands are related to oxygen vibrations. Moreover, the presence of a clear molecular unit (i.e., $(PO_4)^{3-}$) facilitates a simple classification of the bands according to the vibrations of the $(PO_4)^{3-}$ tetrahedral free ion [29] as it is listed in Table 1 (see also Fig. 3a).

Band assignment	Rhabdophane-type structure		
	Present work (cm ⁻¹)	Ref. [30] (cm ⁻¹)	Ref. [31] (cm ⁻¹)
	227	226	228
	383	377	376
PO ₄ –bending $\square_2$	418	413	414
	468	466	466
	547	544	545
PO ₄ –bending $\square_4$	575	573	575
	626	624	625
PO ₄ –symmetric stretching ν_1	974	974	977
PO ₄ –asymmetric stretching ν_3	1027	1029	1039
	1049	1049	
	1086	1084	1085

Table 1. Raman bands observed for the as-prepared rhabdophane-type $LaPO_4 \cdot nH_2O$. Data reported for $LaPO_4 \cdot nH_2O$ obtained by other synthesis methods [30,31] are also included for comparison.

Both, the as-prepared undoped powders after calcination at 950°C for 15 min and doped ones crystallized in the monoclinic space group $P2_1/n$ with 4 molecules per

unit cell ($Z = 4$). There is thus a drastic symmetry loss, although however with gain of inversion symmetry. All the ions are located at lower symmetry sites (Wyckoff positions 4e) and can participate in all modes, which are now $18A_g+18B_g$ Raman modes ($17A_u+16B_u$ are the infrared modes, and $1A_u+2B_u$ are the acoustic modes). Thus, the number of expected Raman peaks increases. The Raman spectrum for calcined $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ confirms a greater number of peaks, which are also better defined. Table 2 (see also Fig. 3) lists the peak wavenumbers observed for the monazite-type LaPO_4 (a) calcined at 950°C for 15 min) and (b) for the as-prepared $\text{La}_{0.975}\text{Sr}_{0.025}\text{PO}_3.988$. Data reported for single crystals of LaPO_4 [30,31] are also included for comparison. The more significant changes in relation to the as-synthesized undoped sample are the greater number of low frequency peaks (below PO_4 bending) caused by the low symmetry of La^{3+} site, so that these ions can participate in 6 modes ($3A_g+3B_g$), as well as the splitting of the PO_4 symmetric stretching peak ($972 \rightarrow 968$ and 993 cm^{-1}) [32].

Band assignment	Monazite-type structure		
	Present work (cm^{-1})		Refs. [30,31] (cm^{-1})
	(a)	(b)	
			90
			100
			151
			157
		173	170
	195	184	184
			219
	227	223	226
		259	258
	272	272	275
		305	
PO_4 – bending ν_2	336		
	395	396	396

		412	413
	467	465	466
	540	540	534
	569	562	567
		571	587
PO ₄ –bending ν_4	592	592	
	621	619	620
	680		
	968	967	968
PO ₄ –symmetric stretching ν_1	990	988	987
	1032		1021
PO ₄ –asymmetric stretching ν_3	1056	1055	1054
	1072	1073	1070
	1191		

Table 2. Raman bands observed for the monazite-type LaPO₄ (a) calcined at 950°C for 15 min) and (b) as-prepared La_{0.975}Sr_{0.025}PO_{3.99}. Data reported for LaPO₄ obtained by other synthesis methods [30,31] are also included for comparison.

Bands corresponding to La(PO₃)₃ (680 and at 1191 cm⁻¹) [33,34] were not observed for any composition and for any studied calcination temperature. Those results are in agreement with those obtained by IR.

Fig. 3. Raman spectra of the (a) as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$, (b) as-prepared $\text{La}_{0.975}\text{Sr}_{0.025}\text{PO}_{3.988}$, and (c) $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ calcined at 950°C for 15 min, i.e., LaPO_4 .

In addition, it can be observed that the Raman peaks are at similar wavenumbers for both undoped and doped monazite phase (powders at any calcination temperature), which can be due to the quite similar radius of Sr^{2+} ion in relation to that of La^{3+} ion.

3.2. DTA-TG studies

A total weight loss of 12.2 wt.% is observed from room temperature up to 1400°C for the undoped sample taking place in different events (Fig. 4a). The first weight loss is produced below 142°C and corresponds to the release of physisorbed water molecules on the powder surface. The second weight loss between 142 and 221°C corresponds to the elimination of chemisorbed water. Both weight losses are associated with two endothermic peaks (Fig. 4a') whose maxima are at 28 (1 in Fig. 4a') and 196°C (2 in Fig. 4a'), respectively. In addition, the weight losses taking place between 120 and up to 280°C are related to the melting (170°C) and partial decomposition (280°C) of the residual NH_4NO_3 [35,36], byproduct of the synthesis reaction [10]. These last two events would have a little contribution to the two endothermic peaks mentioned

above. A third weight loss between ~220 and 600°C corresponds to the progressive dehydration of the rhabdophane phase in accordance with Lucas et al. [37] At 710°C, a very small exothermic peak (3 in Fig. 4a') is observed and is associated to the structural transition from the rhabdophane to the monazite-type structure of LaPO₄. This is confirmed by XRD, IR, Raman, and TEM pictures performed on calcined powders at 725°C for 1 min (see Fig. 6a).

According to Lucas et al. [37] a polytrioxophosphate (La(PO₃)₃) can be formed from the residual (NH₄)₂HPO₄ adsorbed at the particle surface of the synthesized powders. The formation of that tryoxophosphate involves reactions that imply associated weight losses [37] that can be then in part overlapped with the dehydration process of the initial LaPO₄.*n*H₂O. Lucas et al. [37] detected from 1050 and up to 1400°C a weight loss of 1 wt.% caused by the volatilization of a certain amount of P₄O₁₀ gas during the incongruent melting of La(PO₃)₃ that can be present in the samples, according to the following reaction:

In this study continuous weight losses are detected from ~1000°C and up to 1400°C that could be associated to the above mentioned reactions including P₄O₁₀ volatilization process. In particular, for the undoped sample an endothermic peak centered at 1280°C is detected and could be assigned to the decomposition of La(PO₃)₃. It is also in agreement with the phase diagrams in the system La₂O₃-P₂O₅ established by Park and Kreidler [16], Kropiwincka and Znamierowska [17], and Hatada et al. [18]. The progressive weight loss can be due to new lanthanum tryoxophosphate forms as Bregiroux et al. [15] states.

Fig 4b and 4b') shows the DTA and TG analysis, respectively, of the sample with x = 0.05. A total weight loss of 10.2 wt.% from room temperature up to 1400°C, taking also place in different events, is observed. A first weight loss of 2 wt.% from room temperature to 210°C and complemented by a wide endothermic event in the DTA curve centered at 52°C (1 in Fig. 4b') corresponds among other events to the desorption of physically adsorbed water. The second weight loss from 210°C corresponds to the elimination of chemisorbed water. This latter weight loss can be also associated with an endothermic peak whose maximum is at 242°C (2 in Fig. 4b'). Part of this weight loss can be also associated to the residual nitrate elimination from the precursors and from the NH₄NO₃, byproduct formed during the synthesis, as it is mentioned above. The

weight loss associated to the decomposition of $\text{La}(\text{PO}_3)_3$ to LaPO_4 with loss of P_4O_{10} is larger in the doped powder. In addition, an endothermic peak at 1155°C (3 in Fig. 4b') associated to that process is observed for the doped sample. The larger weight loss produced can be due to a larger P/La ratio in that sample. Then, it can be inferred that Sr^{2+} doping enhances the formation of the tryoxophosphate.

Fig. 4. TGA (solid line with a) and b)) and DTA (dashed line with a') and b')) curves obtained in air for the as-prepared powders just milled (a) $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and (b) $\text{La}_{0.95}\text{Sr}_{0.05}\text{PO}_{3.975}$.

3.3. Morphological characterization (TEM and HREM-XEDS) of the as-prepared and calcined powders

The just-milled undoped powders consist basically of needle-like shape nanometric particles (Fig. 5a), typical of the rhabdophane phase and similar to rhabdophane particles obtained from aqueous precipitation [10] or mechanical milling from $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and Na_2HPO_4 [14]. As it is mentioned above, the strontium atoms with further milling provoke a phase transition in the synthesis method employed in this

study since monazite phase is attained in the just-milled powders. It also produces a change in morphology from needle-like to round-shaped particles (Fig. 5a) and b)) in the same way than the calcination process (Fig. 6a) and b)). Needle-like morphology seems to be typical for the rhabdophane phase independently of the synthesis method employed [11,14,38] (Fig. 5a). On the contrary, round-shaped morphology seems to be typical for the monazite-LaPO₄ phase [10,14], when additives that can change the morphology are not employed [25]. The SAED diagrams shown as insets in each micrograph provide also a direct evidence of the microstructure of the materials. Thus, in Fig. 5a) and b) typical diffraction patterns of polycrystalline samples (diffraction rings instead of well-defined spots) are observed.

Fig. 5. Bright-field-TEM micrographs obtained for the samples just milled and dried at 120°C for 4 h (a) as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ and (b) as-prepared $\text{La}_{0.975}\text{Sr}_{0.025}\text{PO}_{3.988}$. Selected area electron diffraction patterns are shown in the insets.

Fig. 6a) shows nanorods and round-shaped nanoparticles when the undoped sample is calcined at 725°C for 1 min indicating that the phase transformation is in progress, according to the DTA-TG analysis. Thus, during the thermal treatment the $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ nanorods transform into round-shaped crystals due to the hexagonal to monoclinic phase transition. Meanwhile, doped powders, both as-prepared and calcined samples (725°C for 1 min), present round-shaped nanoparticles (Fig. 6b). The SAED diagrams shown as insets in each micrograph provide also a direct evidence of the microstructure of the materials.

Fig. 6. Bright-field-TEM micrographs obtained for the (a) undoped sample and (b) for $\text{La}_{1-x}\text{Sr}_x\text{PO}_{4-x/2}$ where $x = 0.05$ ($\text{La}_{0.950}\text{Sr}_{0.050}\text{PO}_{3.975}$) calcined at 725°C for 1 min. SAED patterns are shown in the insets.

In order to confirm the presence of any amorphous phase derived from the polytrioxophosphate TEM-SAED-XEDS analyses for powders treated with an extended heating of 12 h at 800°C were performed. Fig. 7a) and b) show the bright-field HREM images of the undoped and doped sample ($x = 0.05$) respectively, after calcination at 800°C/12 h. Totally clean or much cleaner boundaries of amorphous phase were observed for undoped calcined samples (Fig. 7a). The fringe spacing of the (200) plane is 0.564(2) nm (Fig. 7b) which corresponds with that reported for the base-centered orthorhombic $\text{La}(\text{PO}_3)_3$ structure (PDF card 033-0717; interplanar spacing values $d_{(200)}=0.56500$ nm). The inset at the top of Fig. 8b) corresponds to the SAED pattern at the boundaries of the crystals and reveals an amorphous pattern. XEDS analysis of those regions indicates the presence of La, P and O elements in the sample in an average compositional ratio of La:P:O 58:17:25 (in wt.%) that corresponds to LaPO_4 . Those observations could demonstrate the occurrence of the incongruent melting of the polytrioxophosphate (crystalline area) during the heat treatment at lower temperatures than 877°C [16] if the powders are subjected at extended heating times. When Sr^{2+} is present the P/La ratio increases and it enhances the formation of $\text{La}(\text{PO}_3)_3$ and for that reason is easier to find the amorphous phase at the boundaries in those powders.

Fig. 7. Bright-field high-resolution electron microscopy micrographs of the powder with $x = 0$ (LaPO_4) (a) and $x = 0.05$ ($\text{La}_{0.950}\text{Sr}_{0.050}\text{PO}_{3.975}$) (b) both calcined at $800^\circ\text{C}/12$ h. The inset at the top of the figure b) shows the corresponding selected area electron diffractometry (SAED) patterns taken on an amorphous area of the sample.

3.4. Dilatometric studies

Dilatometric studies reveal that the maximum shrinkage rate is produced at 1210.6°C for the undoped sample (Fig. 8a). However, for those doped a shift at lower temperatures, up to 1002 and 962.3°C for $x = 0.025$ and 0.05 respectively, is observed. Furthermore, linear shrinkage curves show the powders reaching full densification at temperatures of $\sim 1260^\circ\text{C}$ for the undoped sample and up to $\sim 1050^\circ\text{C}$ (for $x = 0.05$) when grain growth becomes dominant. The derivative curves show a peak at temperatures higher than 1300°C that can be related to the above mentioned process of volatilization of P_4O_{10} gas and recrystallization of monazite [11,37]. More in detail, as Fig. 7a) shows the first volume contraction below 150°C can be assigned to the elimination of residual H_2O molecules due to incomplete drying as observed in the TG

curve. The second step at $\sim 300^\circ\text{C}$ can be assigned to the dehydration of rhabdophane yielding hexagonal LaPO_4 with different water contents (from $\sim 300^\circ\text{C}$ to $\sim 600^\circ\text{C}$). It is partially due to the decomposition of residual ammonium nitrate and subsequent volatilization of the corresponding nitrogen oxides. The fourth peak found in the derivative plot centered at $\sim 710^\circ\text{C}$ is associated with the transformation of hexagonal rhabdophane to monazite, according to the DTA-TG analysis. This phase transformation implies a 22% increment in density, from 4.148 to 5.078 g cm^{-3} (densities calculated from XRD data) and produces a more compact atomic arrangement. The step which is the real sintering process starts at around 900°C and is completed at $\sim 1260^\circ\text{C}$ when grain growth becomes dominant. In addition, two more peaks are observed at higher temperatures, one shoulder at $\sim 1380^\circ\text{C}$ and the last peak centered at $\sim 1416^\circ\text{C}$. They are associated to the volatilization of a certain amount of P_4O_{10} and the recrystallization of pure monazite (LaPO_4) [11,39] from the incongruent melting of lanthanum metaphosphate, $\text{La}(\text{PO}_3)_3$, present in the powders. Furthermore, a total shrinkage of a 23.2% of the total length is detected.

In Fig. 8b), two slopes are observed in the shrinkage for the doped samples accordingly, one peak corresponding to the progressive sintering process was observed in the derivative one; from ~ 925 and 870°C (for $x = 0.025$ and 0.05 , respectively), temperature at the shrinkage started, and when the temperature increases a large shrinkage (27.4 and 28.0% for $x = 0.025$ and 0.05 , respectively) of the total length was detected from that temperature up to 1500°C . Then, the effect of Sr^{2+} doping on the dilatometric behavior shows that there is not any peak indicating the hexagonal-monoclinic transformation, as it is mentioned above and according to the DTA-TG results. Moreover, the dilatometric studies reveal that the maximum shrinkage rate is shifted at lower temperatures when Sr^{2+} is present, lower with larger Sr^{2+} content, and is related to the presence of oxygen vacancies (= pyrophosphate groups $\text{P}_2\text{O}_7^{4-}$ at 1262 cm^{-1} observed by IR). In addition, the presence of $\text{La}(\text{PO}_3)_3$ accelerates the densification process since acts as a sintering aid [15]. Furthermore, peaks are observed at higher temperatures than 1300°C that can be explained by the volatilization of a certain amount of P_4O_{10} and the recrystallization of pure monazite (LaPO_4) from the incongruent melting of lanthanum metaphosphate, $\text{La}(\text{PO}_3)_3$, present in the powders [11,27,37]. The greater intensity of the peaks can be due to a larger amount of $\text{La}(\text{PO}_3)_3$ in the doped samples since Sr^{2+} doping implies a larger P/La ratio in those samples and it seems to

enhance the formation of the tryoxophosphate. This result agrees well with those obtained by DTA-TG analysis.

Fig. 8. a) Dilatometric curves: shrinkage vs. temperature (solid line) and shrinkage rate vs. temperature (dashed line) recorded during heating of a green pellet of the undoped sample (as-prepared $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$), and **(b)** of the green pellets of as-prepared

3.5. FEG-SEM-XEDS of samples after dilatometric tests

Dense ceramics with polygonal grains and bimodal grain size distributions were observed on fracture surfaces by FEG-SEM for both undoped (Fig. 9a) and doped samples (Fig. 9b) after the dilatometric tests. For the undoped samples, the grains with the largest size have an average size of $3.0 \pm 0.1 \mu\text{m}$, meanwhile the grains with the smallest size have an average size of $1.5 \pm 0.1 \mu\text{m}$. For the doped samples, the grains with the largest size have an average size of $4.0 \pm 0.1 \mu\text{m}$ (for $x = 0.05$), meanwhile the grains with the smallest size have an average size of $1.0 \pm 0.1 \mu\text{m}$ (for $x = 0.05$). According to FEG-SEM-XEDS in the doped samples the smaller grains do not present Sr in their composition. Those grains can be derived from the recrystallization of LaPO_4 from $\text{La}(\text{PO}_3)_3$. Furthermore, it seems that there is a slightly larger amount of small grains in the doped samples and it may be due to a larger amount of $\text{La}(\text{PO}_3)_3$ that can imply a more intense LaPO_4 recrystallization process in the doped samples. The microstructures are homogeneous and the fracture type is mainly considered to be intergranular. In addition, porosity is not observed.

In addition, the observation at higher magnifications on fracture surfaces of LaPO_4 and Sr^{2+} -doped $\text{LaPO}_{4-x/2}$ shows layered microstructures within grains (Fig. 10). This type of microstructure is due to a plastic deformation of LaPO_4 or $\text{La}_{1-x}\text{Sr}_x\text{PO}_{4-x/2}$ during fracture occurrence. These observations agree well with the fractures observed by Wang et al. [40] for sintered LaPO_4 prepared by mixing phosphoric acid with lanthanum oxide. Either second phases or melts are not observed in the microstructures of the sintered samples at 1500°C presented in this study unlike previous works where Sr^{2+} -doped LaPO_4 powders prepared by precipitation and sintered at lower temperatures showed second phases with formula $\text{Sr}_3\text{La}(\text{PO}_4)_3$ [3,4] distributed in the matrix and $\text{Sr}_2\text{P}_2\text{O}_7$ at the triple points [4,7].

Fig. 9. Fresh-fracture surfaces of (a) LaPO_4 pellet and of (b) $\text{La}_{0.95}\text{Sr}_{0.05}\text{PO}_{3.975}$ pellet after a dilatometric experiment up to 1500°C .

Fig. 10. Detail of the fresh-fracture surface of $\text{La}_{0.95}\text{Sr}_{0.05}\text{PO}_{3.975}$ after a dilatometric experiment up to 1500°C .

When sintering is performed at lower temperatures (1000°C for 1 h) although a bimodal grain size distribution is also observed, the samples present a quite Sr^{2+} homogeneous distribution independently on the grain size. Fig. 11 shows the microstructure of LaPO_4 after sintering at 1000°C for 1 h.

Fig. 11. Fresh-fracture surface of a LaPO_4 pellet after sintering at 1000°C for 1 h.

Monazite-type LaPO_4 is the only phase identified by XRD in all samples after sintering as shown in Fig. 12a) and b). Furthermore, observed d-spacings for both Sr^{2+} -substituted compositions with $x = 0.025$ and $x = 0.05$ are almost identical to that of the undoped monazite phase which is not unexpected since the ionic radii of both Sr^{2+} and La^{3+} cations are quite similar. The effective ionic radii of Sr^{2+} (coordination number = VIII) is $1.26 \text{ \AA}$ and of La^{3+} (coordination number = VIII) is $1.18 \text{ \AA}$ [41,42]. A similar result has been observed in previous works for similar nominal compositions but using other synthesis routes [10,43]. These results agree well with Raman observations where any shift is observed when the samples are doped.

Fig. 12. XRD patterns of (a) LaPO_4 (a) and (b) $\text{La}_{0.975}\text{Sr}_{0.025}\text{PO}_{3.9875}$ after the dilatometric tests.

Then, this method provides a direct, simple and economical route to obtain dense $\text{La}_{1-x}\text{Sr}_x\text{PO}_{4-x/2}$ materials free of second phases containing strontium.

3.4. Electrical characterization

It is well-known that Sr^{2+} -doping promotes proton conductivity in monazite- LaPO_4 [2,4,5,7] and lanthanum polyphosphate [44]. For this study the samples with a largest Sr^{2+} content were selected since according to previous studies [2,4,5,7], the total conductivity in Sr^{2+} -doped LaPO_4 samples increases with increasing Sr^{2+} content at least up to 8% [7]. Fig. 13 shows the total conductivity data versus the inverse of the temperature of $\text{La}_{1-x}\text{Sr}_x\text{PO}_{4-x/2}$ ($x = 0.05$) sintered at 1000°C for 1 h and at 1500°C without any dwell time under dry and wet air. In agreement with previous studies [2,4,5,7], the total conductivity can be interpreted as being dominated by p-type electronic conductivity at the highest temperatures, while a protonic conductivity contribution takes over at lower temperatures and higher water vapor pressures. The

bend in the protonic contribution is assigned to the protons concentration, which saturates at lower temperatures and decreases as temperatures above the bend. The total conductivity is higher for the samples sintered at 1000°C for 1 h. It can be due in part to the LaPO_4 recrystallization process that takes place at a greater extent at high temperatures and provokes the absence of Sr^{2+} in the recrystallized (smaller) grains of the sample sintered at 1500°C, as it is observed by FEG-SEM- XEDS. It implies a heterogeneous distribution of oxygen vacancies that hinders the charge transport. This latter fact together with the presence of $\text{La}(\text{PO}_3)_3$ and the density of grain boundaries should take into account in order to design this type of materials if they are used as proton conductors. Thus, low sintering temperatures are better for the achievement of samples with a more homogeneous composition and then for better electrical properties.

Fig. 13. Arrhenius plots of the total conductivities of $\text{La}_{0.95}\text{Sr}_{0.05}\text{PO}_{3.975}$ ($x = 0.05$) after sintering at 1000°C for 1 h or at 1500°C without any dwell sintering.

4. Conclusions

Rhabdophane-type $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$ nanorods have been prepared by dry mechanical milling and then, the effect of Sr^{2+} addition on the presence of second

phases, the sintering behavior, the microstructural development, and the electrical properties has been studied. When Sr^{2+} is present monazite-type $\text{La}_{1-x}\text{Sr}_x\text{PO}_4$ ($x = 0.025$ and 0.05) nanopowders were obtained instead of rhabdophane-type $\text{LaPO}_4 \cdot n\text{H}_2\text{O}$. The P/La ratio slightly increases for doped samples and it enhances the formation of $\text{La}(\text{PO}_3)_3$ according to DTA-TG, dilatometric studies, and HREM-SAED-XEDS analyses. Weight losses at high temperature are related to the decomposition of $\text{La}(\text{PO}_3)_3$ to LaPO_4 with loss of P_4O_{10} . Dilatometric studies reveal that the maximum shrinkage rate is at 1210.6°C for the undoped samples. However, for those doped there is a shift at lower temperatures (up to 962.3°C for $x = 0.05$) due to the presence of oxygen vacancies, i.e., pyrophosphate groups ($\text{P}_2\text{O}_7^{4-}$) and $\text{La}(\text{PO}_3)_3$. Dense monazite-type $\text{La}_{1-x}\text{Sr}_x\text{PO}_{4-x/2}$ ceramics have been obtained at 1000°C for 1 h and after dilatometric essays at 1500°C without any dwell time in air. Polygonal microstructures with bimodal grain size distributions can be observed for all the materials after sintering although the precursor nanopowders present different morphologies. In addition, the small grains analyzed in the doped samples after the dilatometric tests do not present Sr in their composition due to those grains can correspond to recrystallized LaPO_4 from $\text{La}(\text{PO}_3)_3$. Furthermore, small grains of LaPO_4 are slightly more abundant in the doped samples. It can be related to a larger amount of $\text{La}(\text{PO}_3)_3$ in the Sr^{2+} containing samples. Second phases containing Sr^{2+} are not observed for the doped sintered samples at any studied temperature. Finally, the total conductivity of the studied samples ($x = 0.05$) is higher for the samples sintered at 1000°C for 1 h without any dwell time. It can be due in part to the fact that in the samples sintered at 1500°C the smaller grains do not contain Sr and it hinders the charge transport.

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