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Synthesis and characterization of the solid ionic conductor $La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$.
Síntesis y caracterización del conductor iónico $La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$.

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Resumen

El perfeccionamiento de los dispositivos de almacenamiento de energía es una de las principales líneas de investigación en la actualidad. En este trabajo se realiza un estudio experimental de materiales relacionados con la construcción de baterías sólidas de litio. Para estos fines se sintetizó el óxido mixto $La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$ empleando el método cerámico. La caracterización estructural se realizó por la técnica de difracción de rayos X. Para la caracterización eléctrica del material $La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$ se utilizó la técnica de Polarización Eléctrica en Estado Sólido y el cálculo del coeficiente Seebeck. Las muestras presentan estructura cristalina tipo perovskita, con grupo espacial Pmmm. Las medidas eléctricas demuestran conducción iónica de litio y ausencia de conductividad electrónica.

Palabras clave: Conductores iónicos de litio, coeficientes Seebeck, perovskitas, baterías de litio.

Abstract

The improvement of storing energy devices is an important subject in present days. This paper deals with materials that potentially could be employed as solid electrolytes in secondary lithium batteries. The complex oxide $La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$ was prepared by a ceramic method. The structural characterization was carried out by X ray powder diffraction and electric properties were analyzed by Electric Polarization in Solid State technique and the Seebeck coefficient calculus. The obtained solids have orthorhombic perovskite-like crystalline structure and they are ionic conductors of lithium ion whereas electronic conduction is absent.

Keywords: Lithium ion conductors, Seebeck coefficient, perovskites, Lithium batteries.

Introduction:

The electric properties of ionic conductors with general formula $RE_{0.67-x}Li_{3x}TiO_3$ (RE: La, Pr, Nd, Sm) have been intensively studied owing to their potential applications in solid state batteries (Fortal'nova 2009, 1987; Knauth 2009, 911; Vijayakumar 2004, 2719; V'yunov 2011, 93). These compounds present a perovskite-like crystal structure, where the RE(III) ions occupy the A position (Stramare 2003, 3974; García 2012, 563). The cation ordering, as well as mechanism of ion motion through the solid, remains topics of some discussion (Stramare 2003, 3974; Ruiz 2005, 3521). The proposed conduction mechanism consists on hopping of the lithium ions from its lattice site to adjacent vacancy across to the so called "bottleneck" formed by four TiO_6 octahedra (Vijayakumar 2004, 2719; García 2012, 563; Bohnke 1996, 21). The maximum bulk conductivity value at room temperature, in the order of 10^{-3} Scm^{-1}, was reported for the composition $Li_{0.34}La_{0.51}TiO_{2.94}$. This composition exhibits the best compromise between number of vacancies and amount of lithium ions (Bohnke 1996, 21). Substitution of another rare earth for La decreases the conductivity. This fact is related to the decreasing of unit cell size due to the introduction of a smaller size cation. The reduction of cell parameters shrinks the bottleneck and raises the activation barrier for ionic movement (Martínez 2003, 2458). As a rule, none of these substitutional related solids improve the maximum conductivity value previously reported.

Recently, the solid $La_{0.45}Ce_{0.1}Li_{0.27}TiO_3$ was synthetized by a sol-gel method (Fernández 2012, 59). Substitution of Ce(IV) for La(III) creates additional vacancies and must facilitate the ionic diffusion movement through the solid and hence could improve its conduction properties, despite of the expected bottleneck shrinkage effect. The bulk conductivity obtained at 25 °C was 4.67 x 10^{-4} Scm^{-1} (Fernández 2012, 59), which in order of higher ionic conductors (Bohnke 1996, 21). This paper suggests that rising the Li content in the composition could improve the conduction of the material.

The high cost of the chemicals precursors and the low density of the solid obtained by sol gel method (García 2005,1924) make it advisable to try another method for the synthesis of this kind of Ce(IV) doped solids. Present paper shows the results from synthesizing $La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$ by a traditional solid state reaction ceramic method starting from the oxides and the electrical and structural properties of it.

Experimental Section.

Synthesis: Lithium carbonate (Li_2CO_3 Merck 99.9%), lanthanum oxide (La_2O_3 Aldrich 99.9%) and titanium (IV) oxide (TiO_2 Aldrich 99.9%) were used as starting chemicals. CeO_2 was obtained by thermal decomposition of $(NH_4)_2[Ce(NO_3)_6]$ (Merck 99.9%) at 600 ^{o}C. La_2O_3 and TiO_2 were dried overnight at 900 °C and Li_2CO_3 was dried at 120 ºC during 6 hours prior to weighing. The chemicals were weighed in proper quantities, mixed in an agate mortar with acetone, dried, and heated to 600-700 °C for 2 h to remove CO_2. After ground up, the samples were pressed into pellets placed in folded platinum foil containers, covered with powder of the same composition and with another platinum foil as stopper to minimize the loss of lithium during thermal treatments (Martínez 2003, 2458).

The synthesis of $La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$ comprised a first thermal treatment at 1100 ^{o}C during 16 hours, giving green products that were reground, repelleted and heated at 1200 ºC during 14 hours. A third treatment was carried out with the same conditions of the second one (1200 ºC during 14 hours). After the third treatment, the sample is quenched in air to room temperature to stabilize the high-temperature phase.

Crystalline phase identification and lattice parameters were obtained by powder X-ray Diffraction on Bragg-Bretano TUR M62 diffractometer using Cu-K$_\alpha$ radiation ($\lambda = 1.54178$ Å) at 30 kV and 30 mA, the scanning rate was 1°/min in the 2θ range from 0° to 60°. The diffraction data were processed with CELREF Software.

The electric characterization was carried out by the Electric Polarization in Solid State (EPSS) technique and the calculus of Seebeck coefficient at different temperatures. For these purposes was developed a measuring device designed and constructed in laboratory (Pérez 2000, 60). The pelleted disk-shape sample is placed between platinum electrodes and all the arrangement is placed in a controlled temperature furnace. Through those electrodes the electric potential can be measured at different fixed temperatures. In EPSS technique the sample is initially polarized by means of an DC electric pulse and then is allowed to relax while the electric potential between faces of the sample is measured on time. In order to calculate the Seebeck coefficient (Pérez 2000, 60) a temperature gradient is created between faces of the sample and the resulting electric potential is measured at fixed temperatures.

Results and discussion:

The diffraction pattern obtained for $La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$ is shown in figure 1.
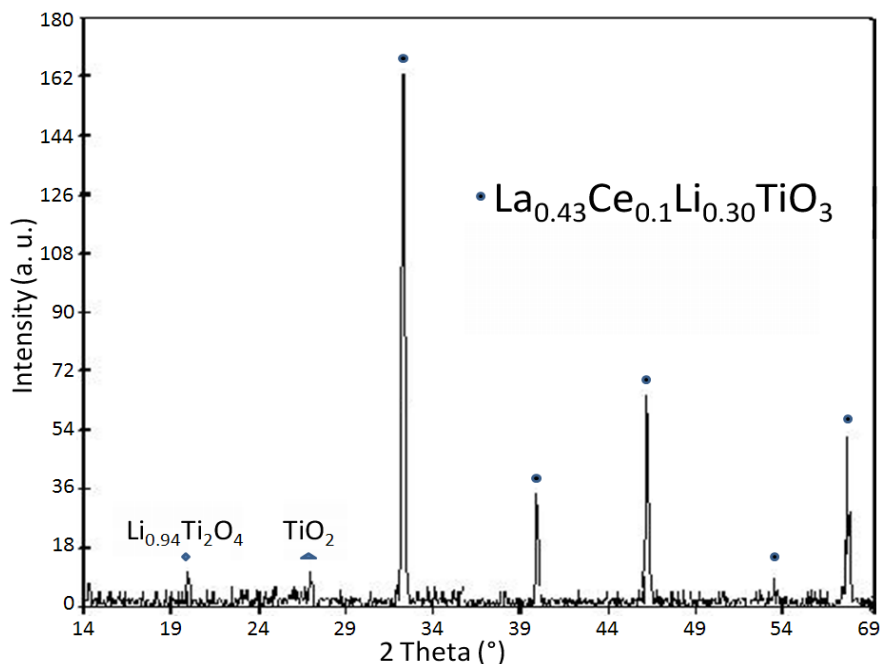
Figure 1. XRD pattern of $La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$.

The main peaks obtained were indexed according to an orthorhombic perovskite-like structure with spatial group Pmmm. Note that this structure is different to the tetragonal in reference (Fernández 2012, 59) as the low temperature sol–gel synthesis leads always to the tetragonal polymorph. This transformation ortorhombic-tetragonal is reversible and it is associated with the A-site cation ordering (Martínez 2003, 2458). Table I shows the position and hkl index resulting from experiment and CELREF Software refining. Two peaks with low intensity at 20.2° and 27.5° are observed in figure 1 correspond to $Li_{0.94}Ti_2O_4$ (PDF # 880609) and titanium oxide (PDF # 894920), respectively. Both impurities appear due to lithium lost, despite of taken precautions, in the high temperature and long time thermal treatments. Lithium lost, attributed to lithium sublimation as LiO_2, has been reported at temperatures as low as 700 °C (Pfeiffer 2005, 1704).

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Table I. Miller indexes and 2θ values (observed and calculated) for $La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$.

hkl	2θ Obs. (°)	2θ Cal. (°)
012	32.706	32.709
112	40.363	40.357
020	46.959	46.948
121	54.296	54.307
212	58.412	58.411

The cell parameters calculated from the diffraction data are a = 3.8690(4) Å; b = 3.8706(5) Å and c = 7.746(2) Å. This values are lower than the reported values for orthorhombic $La_{0.57}Li_{0.27}TiO_3$ (a = 3.8801(3) Å, b = 3.8723(3) Å and c = 7.7747(6) Å) (Inaguma 1997, 105). The apparent smaller unit cell size for the Ce(IV) doped LLTO compared to the doped one is in agreement with the expected effect caused by the replacement for La(III) by the smaller cation Ce(IV). Note that the obtained cell volume (V = 115.9 $Å^3$) is in the order to the obtained for $La_{0.45}Ce_{0.1}Li_{0.27}TiO_3$ (V = 115.2 $Å^3$) (Fernández 2012, 59), despites the differences in composition.

**Electric properties.**

Table II shows the experimental values of Seebeck coefficient (Θ) for $La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$ at different temperatures (T) and temperatures gradients (ΔT).

Table II Seebeck coefficient (Θ) for $La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$.

T(^{o}C)	ΔT(K)	V(mV)	Θ(mV/K)
150	50	15.0	0.30
200	100	34.8	0.35
300	40	10.8	0.27
350	20	7.01	0.35

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High temperature gradients (ΔT) between electrodes were needed at low temperatures to obtain measurable values of electric potential, revealing the small conductivity of material. This result is tipical in ionic conductors (Pérez 2000, 60). The positive sign of Seebeck coefficient (Θ) shows the positive nature of predominant charge carries in the sample. The nearly constant value of Θ for different temperatures indicates that the charge carriers are not thermally activated. These result allows distinguishing the cationic nature of charge carriers from the possible hole carriers conduction. The number of cationic charge carriers is independent of temperature variations whereas the number of holes is strongly dependent on temperature. This is an important result as cerium compounds tend to have electronic conductivity by polarons (Ce ions can change the valence from IV to III), which affect the potential applications of these materials (García 2008, 034105).
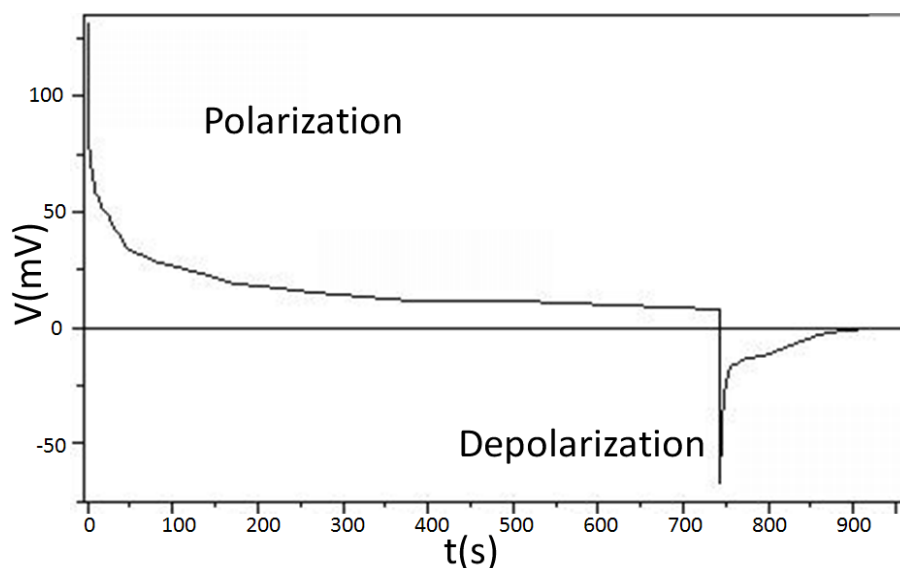
Figure 2. Polarization-depolarization curves for La$_{0.43}$Ce$_{0.1}$Li$_{0.30}$TiO$_3$ at 350 ºC.

The EPSS measurements at low temperatures were unsuccessful because of low conductivity of searched material and insufficient sensitivity of measuring device. This behavior is consistent with Seebeck coefficient experiment results.

Figure 2 shows the polarization-depolarization curves (potential V vs time t) obtained from EPSS technique at 350 ºC. A polarization pulse was applied to the sample, and at 750 seconds the voltage was removed. The material is initially strongly polarized and the voltage curve slowly diminishes to a fixed value that represents the residual polarity. This residual polarity is

indicative of lithium ions blocked at the platinum electrodes, indicating lithium conduction in the material. Removing the initial pulse a similar curve is obtained, but not residual polarization is observed.

The asymmetry found in the depolarization curves of Figure 2 could be related to the presence of some lithium cations in different positions in the crystal lattice, which could be modified during the first forced polarization step and further relocation of ions during depolarization along the experiment. Some previous reports and computational modeling reveal several equilibrium positions for lithium ions in vacancy defective perovskite-like lattice (Ruiz 2005, 3521; Catti 2007, 3963). The obtained results indicate the cationic nature of conduction process and the lack of any appreciable electronic charge transfer.

Conclusions:

$La_{0.43}Ce_{0.1}Li_{0.30}TiO_3$ has been synthesized by traditional ceramic method. XRD shows the Pmmm orthorrombic perovskite structure. Two peaks of low intensity were observed in the XRD pattern, which are associated to $Li_{0.94}Ti_2O_4$ and titanium oxide. The presence of these phases is associated to the lithium losses due to the high temperatures and long times required in this method of synthesis. The obtained cell parameters are according to solids synthesized by sol gel method. The obtained solids are ionic conductors with any detectable electronic component. This is a very important result for future applications in solid state batteries.

Acknowledgements

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