CRYSTALLINE PEROVSKITE $La_{0.67-x}Li_{3x}TiO_3$: PREPARATION AND IONIC CONDUCTING CHARACTERIZATION

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Abstract. *Crystalline perovskite $La_{0,67-x}Li_{3x}TiO_3$ with $x = 0.06$, 0.11 and 0.15 were prepared by solid-state-solution reactions at $1350^\circ C$ from TiO_2, La_2O_3 and Li_2CO_3. Crystalline structure of these compounds was analyzed by XRD method. The ionic conducting property of $La_{0.67-x}Li_{3x}TiO_3$ was characterized on AutoLab.Potentiostat-PGS30 system with impedance technique using fitting software program available in the equipment. The highest ion conductivity at room temperature was found for the compound with $x = 0.11$, namely $\sigma = 3.1 \times 10^{-5} Scm^{-1}$. With increase of temperature the ionic conductivity increased and at $200^\circ C$ it reached a value in two orders in magnitude higher ($6 \times 10^{-3} Scm^{-1}$). The activation energy of the compounds was determined on $Ln(\sigma)$ vs. $1/T$ plots and found to be as low as $0.36\ eV$.*

I. INTRODUCTION

Lithium ion conducting materials have been received increasing interest in the last years because of their potential application in solid state batteries, electrochromic cells [1] and other electrochemical devices [2]. These fast ionic conducting materials served as a non-toxic solid electrolyte exhibit easy preservation and comfortable use. Using these materials enables to simplify devices design, especially for the devices made from thin solid layers like all solid state smart windows or mirrors, thin film batteries, etc. [3-4]. Many previous works have focused onto subject of Li-based solid solutions [3,5] and compounds of spinel structures of $LiMn_2O_4$, LiV_3O_8 [6-7]. These materials have low conductivity even at high temperature, whereas one of the most important requirements for the solid electrolytes is a high long-range ionic conductivity at room temperatures. Among best ionic conductors at room temperature, recently a new family of $La_{(2/3)-x}Li_{3x}TiO_3$ perovskites, with $0.06 < x < 0.167$, have been found. As reported in [3-4] these structures in principal can possess a dc-conductivity as high as 10^{-3} S/cm. In practical works, however, the ionic conductivity has been obtained only in a range of 10^{-10} to 10^{-7} Scm^{-1}, this is because a partial substitution of La by Li and/or substitution of Ti by other tetravalent and pentavalent cations requires much serious experimental effort that can be dedicated to improve lithium mobility. In this work we present recent experimental results obtained on superionic conductors of $La_{0.67-x}Li_{3x}TiO_3$ prepared by solid solution reactions from TiO_2, La_2O_3 and Li_2CO_3 at a temperature of 1350°C.

II. EXPERIMENTAL

The $La_{0.67-x}Li_{3x}TiO_3$ solid solution with $x = 0.06$, 0.11 and 0.15, respectively called M06, M11 and M15, was prepared by conventional solid-state reactions from stoichiomet-

ric amounts of TiO_2(99.95%), Li_2CO_3, (99.97%) and freshly dehydrated La_2O_3 (99.9%) purchased from Aldrich. The starting materials were mixed and pressed into pellets (diameter = 12 mm, thickness = 5 mm, P = 300 MPa), then annealed in platinum crucibles at 800°C for 10 h. After grinding and pressing again, a second heating treatment was performed on smaller pellets (diameter = 10 mm, thickness 1.2 mm, P = 400 MPa) at 1350°C for 8 h. The heating sweep rate is 5°C min^{-1}and the cooling is natural. The crystalline structure has been studied by using X-ray diffraction analysis (XRD) and the molecular structure by Raman scattering spectroscopy. The ionic conductivity of the samples was characterized on AutoLab. Potentiostat-PGS30 using FRA-2 impedance software. To characterize impedance spectroscopy (IS) the samples were mechanically polished and chemically treated in order to have clean and parallel surfaces, then on these surfaces a metallic silver coating with 6 mm-diameter circle was vacuum evaporated. Sintered cylindrical pellets 12 mm in diameter and 1.5 mm thick, with the evaporated silver electrodes, were used for electrical measurements. IS measurements were recorded under normal atmosphere between room temperature (RT) and 200°C, in the frequency range 0.1 Hz to 1.0 MHz.

III. RESULTS AND DISCUSSION

III.1. Crystalline structure

Fig. 1 shows the XRD patterns of samples annealed at 800°C and after heated at 1350°C. From this figure one can see that the partial compounds of solid solution at 800°C have been reacted to form three quasi-stable structures of $La_{0.66}TiO_3$, $Li_2Ti_3O_7$, $La_2Ti_2O_7$ and a small amount of $La(OH)_3$. After quenching at high temperature (1350°C) by the XRD patterns these structures have disappeared, instead, all peaks obtained characterize a single structure phase of $La_{0.67}TiO_3$ (Fig1b). The XRD study of $La_{0.67-x}Li_{3x}TiO_3$ also showed that different patterns were obtained depending on the lithium content in these perovskites. For samples with high lithium contents ($x = 0.11$ and 0.15), XRD patterns could be indexed with the diagonal perovskite cell deduced in a previous microstructures study [8]. However, the average crystal structure deduced from XRD experiments
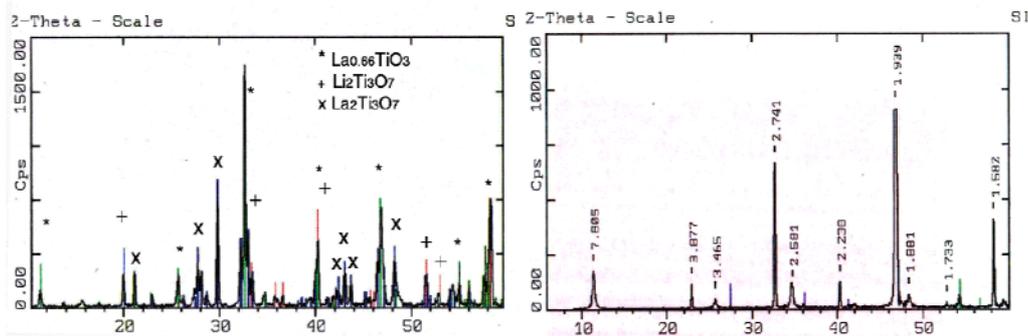
Fig. 1a. XRD patterns of $La_{0.67-x}Li_{3x}TiO_3$ annealed at 800°C for 10 h

Fig. 1b. XRD patterns of $La_{0.67-x}Li_{3x}TiO_3$ heated at 1350°C for 8 h.

could be interpreted with a smaller cell. The best fitting of the XRD patterns was achieved using a primitive $P4/mmm$ tetragonal cell, derived from the cubic perovskite. Note that, in the case of orthorhombic perovskites, peaks of the superstructure are sharper and stronger than those detected in tetragonal phases. In the case of tetragonal samples with $x = 0.11$ a fast cooling from 1350°C produced an XRD pattern without superstructure (Fig. 1b) that could be indexed with a cubic cell (a =3.87 Å).
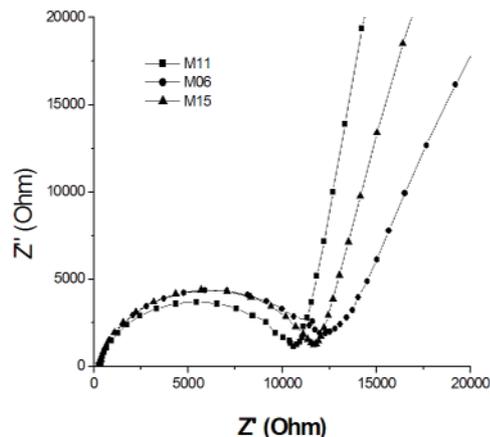
III.2. Ionic conducting property

The experimental IS data of all the samples were fitted by equivalent circuits with their analytical equations. From the fitted curves one can find out the characteristics of the IS curves. In IS measurement, the total macroscopic current flowing in response to an applied potential is measured. This current is the sum of many microscopic currents flowing from one electrode to the other. The origins of these currents are different in nature. The applied potential leads to hopping of the mobile ions into a preferred direction and also to polarization of all the dipoles present or induced in the material. As shown previously, both of these processes are contained in the IS data. These physical processes occur simultaneously and are not totally independent. Indeed the hopping of the mobile ions can modify the polarization of the surrounding dipoles or create new dipoles in the vicinity of the conduction path [9]. A typical presentation of IS characterization for the sample with $x = 0.06$, 0.11 and 0.15 is shown in Fig. 2.

From Fig. 2 one can note that the IS of the sample consists of two characteristic parts. In the range of high frequencies the IS circle is formed due to the ionic conducting, at such high frequencies the electronic conductivity is negligible. The next line of the IS obtained at low frequencies characterizes the ionic diffusion effect in the Helmholtz layer [10]. The ionic conductivity (σ_{Li}) can be thus expressed by the following formula:

Fig. 2. Impedance spectra of $La_{0.67-x}Li_{3x}TiO_3$ samples with different Li-content $x = 0.06$ (●), 0.11 (■) and 0.15 (▲).

$$\sigma_{Li} = \frac{d}{R \times S} \qquad (1)$$

where d is the sample thickness, S - electrodes square and R - bulk resistance.

Li-content dependence of IS is also shown in Fig. 2. The fact that the shape of IS curves of samples with different Li-content is quite similar proves that the equivalent circuit of the electrochemical cells is the same. The part of IS caused by the ionic diffusion effect in the Helmholtz layer is not changed, whereas the part concerning ionic conducting of the samples shifts from middle value of R_2 (for $x = 0.06$) to smaller for $x = 0.11$ and
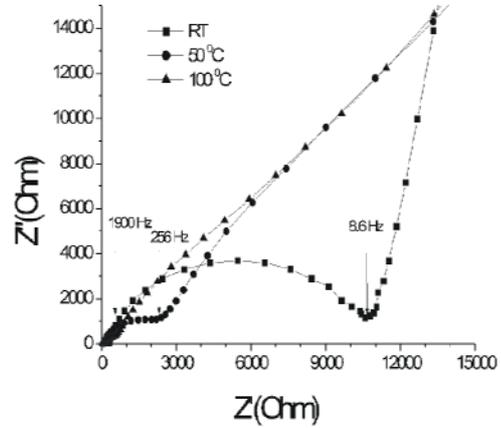
to larger for $x = 0.15$. This means that the optimum content of Li for the best ionic conductivity of $La_{0.67-x}Li_{3x}TiO_3$ was found to be a value corresponding to $x = 0.11$. Calculating σ_{Li} from these fitted curves one can see a clearer dependence of the ionic conductivity on the Li-content (see Table 1).

Table 1. *Conductivity at room temperatue of* $La_{0.67-x}Li_{3x}TiO_3$ *with* $x = 0.06, 0.11$ *and* 0.15

x	0.6	0.11	0.15
σ_{Li} (Scm^{-1})	$1.8\ 10^{-5}$	$3.1\ 10^{-5}$	$2.3\ 10^{-5}$

The Li-content of the ionic conductivity at room temperature is not so strongly demonstrated as that is in high temperature. Through the $\sigma_{Li} \sim T$ curves for above mentioned samples one can calculate not only the active energy for each sample but also the difference between their ionic conductivity (Fig. 3). It is clearly seen that the IS of the compound (x = 0.11) changes strongly with increasing temperature. The IS circle becomes smaller at 50°C and 100°C, moreover this circle finishes at a larger value of the frequency, namely at 3.6, 296 and 1500 Hz, for RT, 50°C and 100°C, respectively. At 100 °C the ionic conductivity reached a value as

Fig. 3. Impedance spectra vs temperature of the $La_{0.67-x}Li_{3x}TiO_3$ sample with $x = 0.11$; RT ($\blacksquare$), $T = 50°C$ ($\bullet$) and $T = 100°C$ ($\blacktriangle$).

high as $2.7 \times 10^{-4} Scm^{-1}$, and at 200°C – as $6 \times 10^{-3} Scm^{-1}$, that is larger in two order in magnitude compared with the conductivity at room temperature. The active energy of the compounds that determined from the $\ln(\sigma) \sim (1/T)$ curve is slight dependent on the Li-content and consists of about $E_a = 0.36$ eV which is consistent with the result recently reported in [4].

IV. CONCLUSION

Ionic conducting perovskite $La_{0.67-x}Li_{3x}TiO_3$ was prepared by solid state solution reactions. Both the XRD structural analysis and the impedance spectra characterization showed that the $La_{0.67-x}Li_{3x}TiO_3$ compound with x = 0.11 has the best ionic conductivity. From the temperature dependence of the ionic conductivity it has been found that the active energy of the compounds is slightly dependent on the Li-content and consists of about 0.36 eV. For x = 0.11, at room temperature the ionic conductivity is as high as σ_{Li} = 3,1 x 10^{-5} Scm^{-1} and increases up to a value of 6 x10^{-3} S cm^{-1} at 200°C - in two order in magnitude larger.

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