

## Raman Scattering Study of $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$ : Relationship between Spectra Parameters and Amount of Lithium

H. M. Omanda,<sup>1,2\*</sup>, H. Gnanga<sup>1</sup>, P. Soulounganga<sup>1</sup>, R. Ondo Ndong<sup>1</sup>, A. Eya'a-Mvongbote<sup>1</sup>, Z.H. Moussambi Membetsi<sup>1</sup> And Alain Bulou<sup>2</sup>

<sup>1</sup>Laboratoire Pluridisciplinaire des Sciences (LAPLUS), Ecole Normale Supérieure  
BP 17009 Libreville, Gabon.

<sup>2</sup>Laboratoire de Physique de l'Etat Condensé (UMR 6087 CNRS), Université du Maine,  
Av. O. Messiaen, 72085 LE MANS Cedex 9, France

### Abstract

*The Raman-active lattice modes in lithium lanthanum titanates  $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$  (LLTO) at room temperature were investigated using a Raman spectrometer of limiting resolution  $0.005\text{ cm}^{-1}$ . Particular attention was paid to search a correlation between Raman parameters (positions, linewidth and peaks intensity spectra) and  $x$  content. The characterization of LLTO by Raman spectroscopy made it possible to identify  $E_g$  modes predicted by the groups theory. The attribution of the modes  $A_{1g}$  and  $B_{1g}$  could not be done in a precise way because the spectra profile obtained is complex. The variations study of the frequencies, the linewidths and the amplitudes according to  $x$  content shows a correlation as regards the vibrations frequencies. We observe a growth of the frequency for the weak concentrations up to  $x=0.10$ , then a decrease for higher rates. This behavior is similar to that observed for the variation of conductivity according to the lithium rate.*

**Keywords:** Lithium Ion conduction, Raman spectroscopy, group theoretical, vibration modes

### 1. Introduction

The series of lithium lanthanum titanates  $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$  (LLTO), solid solution in the perovskite type  $\text{ABO}_3$ , have received a considerable attention since several years. Belous and al.[1] and Inaguma and al.[2] have shown the high ionic conduction of LLTO. It is owing to the lithium ion mobility and vacancies which induce a structural distortion. In addition, it has been reported that lithium lanthanum titanates show high ionic conductivity as high as  $10^{-3}\text{ S cm}^{-1}$  at room temperature [2]. Therefore a particular interest was related to LLTO because of their

potential applications in electrochemical devices such as high-energy lithium ion batteries, electrochromic systems, supercapacitors, and electrochemical sensors[3,4]. In the electrochemical devices, LLTO can be used as electrolyte material in the solid-state batteries[5, 6] or as protecting thin coating against the exothermic phenomena in lithium ion batteries with liquid electrolyte [7].

From a structural point of view, the research undertaken on the LLTO remains discussed as well range of composition  $x$  of the solid solution as crystallographic structure [8-12]. We retain for our study the existence of the solid phase of type perovskite  $\text{ABO}_3$  in the range of composition of  $0.06 < x < 0.14$  with a crystallographic structure of group of space  $P4/mmm$  [9, 11].

In a general way we can note that the structure of  $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$  drifting of a structure perovskite of the lacunar type  $\text{ABO}_3$ , with  $\square$  representing a vacancies, varies according to composition  $x$ , but as of the heat treatment as the material could undergo during its development. Several techniques of syntheses of LLTO are reported by the literature among which deposits in thin layer [2, 8-15].

In order to understand the relationship between the Raman spectra parameters and the  $x$  composition of  $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$ , the measurement were led on seven samples of LLTO in the range  $0.06 < x < 0.14$ .

### 2. Experimental and theoretical analysis

*Preparation of  $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$  sample:* LLTO powder samples were obtained using the procedure of Fourquet et al.[9]: the compositions corresponding to these series were synthesized from stoichiometric amounts of  $\text{La}_2\text{O}_3$ ,  $\text{TiO}_2$ , and  $\text{Li}_2\text{CO}_3$  (high purity grade). The reagents were mixed and pressed into pellets and first heated in air for 4h at  $850^\circ\text{C}$  in

platinum boats. After regrinding and repressing, the samples were heated three times for 10 h at 1150°C and were allowed to cool in furnace (naturally down to 200°C).

**Structural data:** Structural data: The structure of  $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$  series has been studied by Fourquet et al.[9]. They have shown that, at room temperature, all samples of the series can be indexed in a primitive tetragonal cell deriving from the perovskite-type  $\text{ABO}_3$  structure, with a  $c/2a$  distortion decreasing for high lithium content. The space group of primitive tetragonal of LLTO series was assumed to be  $Z=2$ . The unit cell parameters are  $a=a_p=3.87$  and  $c=2a_p$ . The figure 1 shows a schematic view of LLTO and in the table 1 crystallographic data and symmetry point atom in the structural model in the space group  $P4/mmm$  are listed.

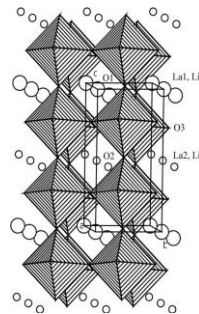


Figure 1: Structure crystallographic of  $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$  in the space group  $P4/mmm$ .

Table 1. Structural Model of  $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$  in the Space Group  $P4/mmm$ [9]

Atoms	Sites	Symmetries	coordinates
La1+Li+□	1a	$D_{4h}$	0, 0, 0
La2+Li+□	1b	$D_{4h}$	0, 0, 1/2
Ti	2h	$C_{4h}$	1/2, 1/2, $z \approx 0.25$
O1	1c	$D_{4h}$	1/2, 1/2, 0
O2	1d	$D_{4h}$	1/2, 1/2, 1/2
O3	4i	$C_{2h}^v$	0, 1/2, $z \approx 0.25$

According to this model, the  $\text{La}^{3+}$  ions are centered in the A-site of the perovskite structure formed by eight  $\text{TiO}_6$  octahedra. On the other hand, if the  $\text{La}^{3+}$  ion location is perfectly defined, the location of the  $\text{Li}^+$  ions has been a matter of debate.

This structure is characterized by a distribution of the vacancies and cation  $\text{La}^{3+}$ ,  $\text{Li}^+$  on the two sites 1a(0, 0, 0) and 1b(0, 0, 1/2). It has been shown that the  $\text{La}^{3+}$  distribution evolves with x content, that the 1a site is favorable to the  $\text{La}^{3+}$  ions, and that the introduction of the  $\text{Li}^+$  ions increases the cationic disorder on site A. The maximum occupancy of  $\text{La}^{3+}$  is observed for a value of  $x=0.08$ , corresponding to the composition with the maximum distortion of the tetragonal unit cell. This model does not take account of  $\text{Li}^+$  and vacancies, it is assumed that they partially occupy both 1a and 1b sites. The  $\text{TiO}_6$  octahedrons are distorted along the c axis.

**Raman Spectroscopy Analysis:** The Raman spectra were recorded on the powder of LLTO using a DILOR Z24 spectrometer. An argon laser (Coherent Innova 90.3) was used for the excitation: radiation of the wavelength 514.5 nm was used. The spectral width (full-width at half-maximum) was less than 6  $\text{cm}^{-1}$  and the error in the line positions was less than 1  $\text{cm}^{-1}$ . The measurements were made at room temperature under a microscope (in the back-scattering geometry) with a X50 objective with a long working distance. This was performed on micrometric samples (typically less than 0.1mm in length) fixed on a goniometer head and suitably orientated for polarization analysis.

**Enumeration of vibration modes:** Using the structural data and the crystallographic tables of the space group [18], we reported on the table 2 the symmetries vibration modes. The mechanical representation is written:

$$\Gamma^{\text{Mechanical}} = 2A_{1g} \oplus 6A_{2u} \oplus B_{1g} \oplus B_{2u} \oplus 3E_g \oplus 7E_u$$

As  $\Gamma^{\text{Mechanical}} = \Gamma^{\text{Acoustic}} + \Gamma^{\text{Optical}}$  and according to the character table of the  $P4/mmm$  group, we have  $\Gamma^{\text{Acoustic}} = A_{2u} \oplus E_u$ , so the optical modes are noted:

$$\Gamma^{\text{Optical}} = 2A_{1g} \oplus 5A_{2u} \oplus B_{1g} \oplus B_{2u} \oplus 3E_g \oplus 5E_u$$

The active vibration symmetries modes into Raman spectroscopy are  $A_{1g}$ ,  $B_{1g}$  and  $E_g$ . We only observed:

$$\Gamma^{\text{Raman}} = 2A_{1g} \oplus B_{1g} \oplus 3E_g$$

Table 2. The symmetry modes in  $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$ .

Atoms	Symmetries vibration modes
La <sub>1</sub> (1a)	$A_{2u} \oplus E_u$
La <sub>2</sub> (1b)	$A_{2u} \oplus E_u$
O <sub>1</sub> (1c)	$A_{2u} \oplus E_u$
O <sub>2</sub> (1d)	$A_{2u} \oplus E_u$
O <sub>3</sub> (4i)	$A_{1g} \oplus A_{2u} \oplus B_{1g} \oplus B_{2u} \oplus 2E_g \oplus 2E_u$
Ti(2h)	$A_{1g} \oplus A_{2u} \oplus E_g \oplus E_u$

We can see that only 6 modes are predict in Raman spectroscopy including  $3E_g$  doubly degenerated modes,  $2A_{1g}$  modes and one  $B_{1g}$  mode. We can notice, as shown in the table 2, that these modes do not give account of the vibrations of the La and Li atoms in this structure, but only Ti and O3 atoms. La, Li and the vacancies represented by La1 and La2 in the structure are related to inactive modes in Raman spectroscopy.

### 3. Results and discussion

The Raman spectra of LLTO are represented in figure 2. We have reported on the table 3 the Raman shift for different x values.

For  $x=0.07$ , it appears four significant peaks located at 139.14, 236.04, 317.6 and 524.9  $\text{cm}^{-1}$ . These peaks are allotted to the vibration modes of the LLTO. Other peaks appear to 567.52 and 781.12  $\text{cm}^{-1}$  after applying of the Fit-Peak program.

For  $x=0.075$ , we find four well-defined peaks to 139.7, 237.25, 318.27 and 523.1  $\text{cm}^{-1}$  like the  $x=0.07$  sample.

On the other hand, very badly defined peaks appeared to 382.31 and 453.83  $\text{cm}^{-1}$ , in addition to those to 564.66 and 780.13  $\text{cm}^{-1}$ , which are comparable with the preceding case. One also observes a series of peaks around the principal line to about 139  $\text{cm}^{-1}$ .

Table 3. Experiment Raman shift for various x content in  $\text{La}_{2/3-x}\text{Li}_{3x}\square_{1/3-2x}\text{TiO}_3$ .

x	$\tilde{\nu}_1(E_g)$	$\tilde{\nu}_2(E_g)$	$\tilde{\nu}_3$	$\tilde{\nu}_4$	$\tilde{\nu}_5(E_g)$	$\tilde{\nu}_6$	$\tilde{\nu}_7$
0.07	139.14	236.04	317.59	455.87	524.90	567.52	781.12
0.075	139.71	237.25	318.27	453.83	523.10	564.66	780.13
0.085	140.07	238.11	318.34	455.86	524.92	570.24	774.83
0.095	141.10	239.00	318.69	452.77	524.38		
0.10	141.64	240.01	320.08	450.37	525.68	571.4	786.24
0.12	143.48	241.03	313.97	453.48	523.33		
0.13	140.62	238.02	316.25	455.96	523.83	558.95	790.91

The  $x=0.085$  sample, we still find the same profile as previously with this time of the lines located at 140.07, 238.11, 318.34 and 524.92  $\text{cm}^{-1}$ . It is noticed that the peaks intensity to 570.24, 774.83 and 455.86  $\text{cm}^{-1}$  have relatively increased compared to the preceding rate.

As in the preceding case the  $x=0.095$  sample for bands are dominating in position 141.11, 238.98, 318.69 and 524.38  $\text{cm}^{-1}$ . The peak to 452.77  $\text{cm}^{-1}$  seems to have

taken amplitude. The other peaks observed on the preceding spectra are also present here.

For the  $x=0.10$  compound, the lines account this time for 141.64, 240.01, 320.08 and 525.67  $\text{cm}^{-1}$ . One always notices the same peaks with the positions equivalent as previously to 450.37, 571.4, and 786.24  $\text{cm}^{-1}$ .

For the  $x=0.12$  sample, One notices a significant displacement of the positions of the peaks compared to the preceding cases. The significant peaks occupy 143.48, 241.03, 313.97 and 523.33  $\text{cm}^{-1}$  position. We always note the presence of a peak with 453.48  $\text{cm}^{-1}$  whose intensity increased compared to the precedents. It is also noticed that the peak to 313.00  $\text{cm}^{-1}$  moved closer to the peak to 241  $\text{cm}^{-1}$ . It is the same observation made for the peak located to 571  $\text{cm}^{-1}$ . This peak is practically confused with that to 523.33  $\text{cm}^{-1}$ . One still finds the profile observed towards 750  $\text{cm}^{-1}$  that previously.

The  $x=0.13$  sample, we found the typical profile observed until  $x=0.10$ . The peaks are allocated to 140.62, 238.02, 316.25 and 523.83  $\text{cm}^{-1}$ . We have peaks to 455.96, 558.95 and 790.91  $\text{cm}^{-1}$ .

Lattice dynamic studies [19, 20, 21] have showed that the lines located on average at 139, 239 and 523  $\text{cm}^{-1}$  can be assigned to the three  $E_g$  modes predicted by the theory of the groups. It is noted that these peaks are well defined for all studied rates. With regard to the other awaited modes, their attributions are discussed because of the broad profiles of the peaks observed. These results are explained by the lattice dynamics[19,20]. It appears indeed that in the case of the  $E_g$  modes, the displacement of the ions is done in perpendicular plans with the axis  $C_4$  of the structure perovskite of the LLTO. These movements around octahedral  $\text{TiO}_6$  do not utilize the sites statistically distributed in ions It and Li or gaps. All occurs as if there were a compact stacking in the plan, which returns the frequencies of vibration of quite visible the  $E_g$  modes in the spectra with rather fine peaks. The displacements associated with the  $A_{1g}$  and  $B_{1g}$  modes are done in the direction of the axis C thus implying the A-site which are occupied at random by La and Li ions or vacancies. This observation can explain the fact that the lines related to these modes appear broadened owing to a dispersion of the interactions between the atoms involved in the movements. The  $A_{1g}$  vibration modes can be allotted to the one of the lines located on average to 318, 455, and 568  $\text{cm}^{-1}$  and the  $B_{1g}$  mode

localization remains more difficult, in accordance with the studies carried out by Laguna et al [19,20].

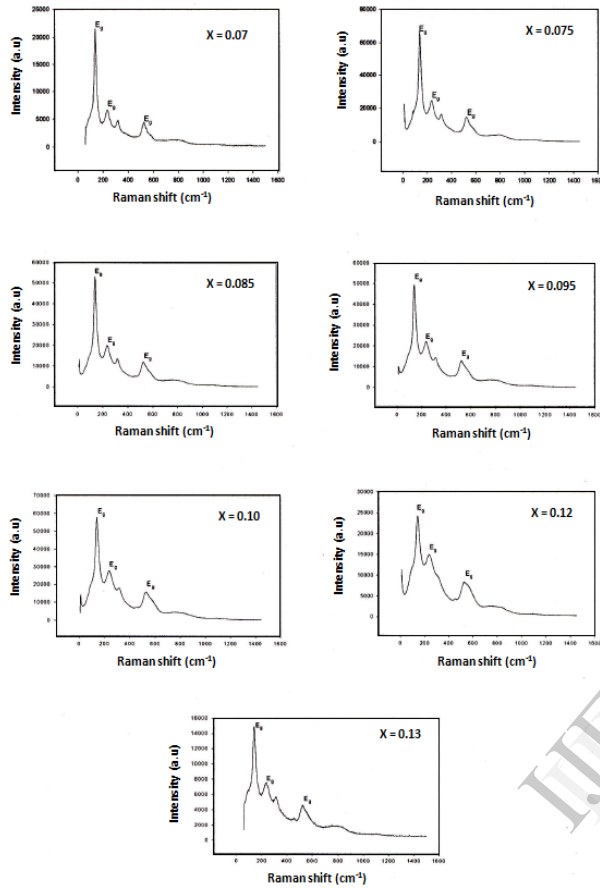


Figure 2: Raman spectra of the  $La_{2/3-x}Li_{3x}\square_{1/3-2x}TiO_3$  from various x values.

The Raman spectra parameters are shown to the figures 3, 4 and 5: vibration frequency positions (fig.3), linewidth (fig.4) and intensity of characteristic peaks (fig.5).

This study shows spectra with nearby profiles, but presenting rather significant variations of frequencies up to  $10\text{ cm}^{-1}$  and width of peaks; there seems to be an extremum for concentrations of x around 0.10. With regard to the amplitudes, one obtains less regular evolutions not being able to give an account of specificities of material. This result could be explained by the fact why during the Raman analysis the fields explored by the beam are very varied from one sample to another and by the possible presence of impurities.

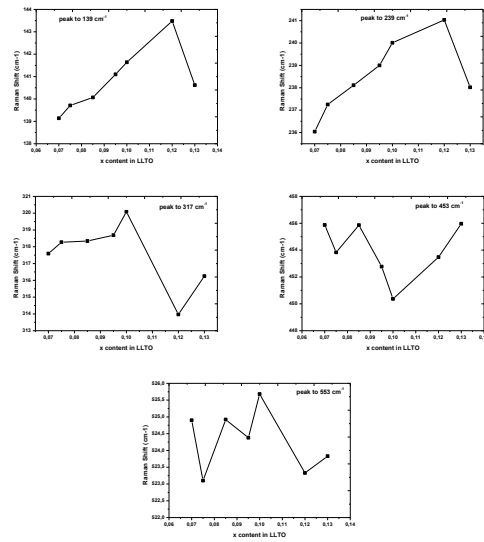


Figure 3: Variation of peaks position versus x content.

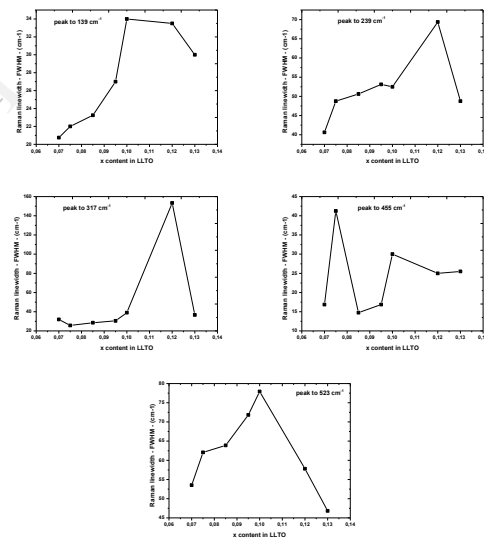


Figure 4: Variation of linewidth (FWHM) of Raman peaks versus x content

In spite of the observation of evolutions of the frequency and width in middle height, those are not regular it would be too early to connect the frequency of vibration of a sample of LLTO to its concentration. But it is not excluded that a more rigorous work makes it possible to bring to the required result.

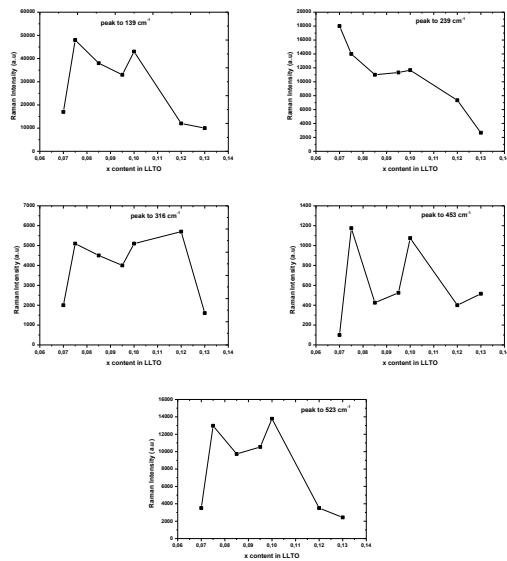


Figure 5: Variation of Raman intensity of principal peaks versus x content

#### 4. Conclusion

In this work, we performed the Raman spectroscopy study of ionic conduction oxides by the ions lithium. Raman spectra of LLTO did not make it possible to clearly identify the six modes awaited by the theory of the groups. However, thanks to a study of lattice dynamics [19,20], we could allot the  $3E_g$  modes to the frequencies located towards 138, 236 and  $524\text{ cm}^{-1}$ . The other modes are not very obvious in the spectra. This result is because in these ionic conducting materials where the non-stoichiometric armature the presence of gaps, the neighborhood of atoms is very variable because of the random distribution of the atoms in the various sites. The analysis of the curves of frequencies, linewidths and amplitudes variations according to rate  $x$  of lithium in LLTO, did not give a great satisfaction. However, for the frequencies variations, we observe the same profile i.e. a growth for the weak concentrations to about of  $x=0.10$ , then a decrease for higher rates. This behavior can be compared with the variation of conductivity [22]. Only thorough studies will be able to say us some more.

#### 5. References

- [1] A. G. Belous, V. I. Butko, G. N. Novitskaya, S. V. Polyanetskaya, Y. M. Poplavko and B. S. Khomenko, Electrical conductivity of the perovskites  $\text{La}_{2/3-x}\text{M}_{3x}\text{TiO}_3$ , *Ukrainskii Fizicheskii Zhurnal* 31, (1986), 576-580.
- [2] Y. Inaguma, C. Liqun, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta and M. Wakihara, High Ionic Conductivity in Lithium Lanthanum Titanate, *Solid State Communications*, Vol. 86, No. 10, (1993), 689-693.
- [3] C. Bohnke, J.-L. Fourquet, Impedance spectroscopy on pH-sensors with lithium lanthanum titanate sensitive material, *Electrochimica Acta* 48, (2003), 1869-1878.
- [4] O. Bohnke, The fast lithium-ion conducting oxides  $\text{Li}_3\text{La}_{2/3-x}\text{TiO}_3$  from fundamentals to application, *Solid State Ionics* 179, (2008), 9-15
- [5] S. Stramare, V. Thangadurai and W. Weppner, Lithium Lanthanum Titanates: A Review, *Chem. Mater.* 15 (2003), 3974-3990.
- [6] Yoshiyuki Inaguma, Liqun Chen Mitsuru Itoh and Tetsuro Nakamura, Candidate compounds with perovskite structure for high lithium ionic conductivity, *Solid State Ionics* 70-71, (1994), 196-202.
- [7] Mitsuru Itoh, Yoshiyuki Inaguma, Woo-Hwan Jung, Liqun Chen, and Tetsuro Nakamura, High lithium ion conductivity in the perovskite-type compounds  $\text{Ln}_{1/2}\text{Li}_{1/2}\text{TiO}_3$  (Ln=La, Pr, Nd, Sm), *Solid State Ionics* 70-71, (1994), 203-207.
- [8] H. Omand, T. Brousse and D. M. Schleich, *New Trends in Intercalation Compounds for Energy Storage*, (2002), 483-487.
- [9] A. Varez, F. Garcia-Alvarado, E. Moran and M. A. Alario-Franco, Microstructural Study of  $\text{La}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ , *Journal of Solid State Chemistry* 118, (1995), 78-83.
- [10] J. L. Fourquet, H. Duroy, and M. P. Crosnier-Lopez, Structural and Microstructural Studies of the Series  $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ , *Journal of Solid State Chemistry* 127, (1996), 283-294.
- [11] J. Ibarra, A. Varez, C. Leon, J. Santamaria, L.M. Torres-Martinez, J. Sanz, Influence of composition on the structure and conductivity of the fast ionic conductors  $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$  ( $0.03 \leq x \leq 0.167$ ), *Solid State Ion* 134 (2000) 219-228.
- [12] Odile Bohnke, Huguette Duroy, Jean-Louis Fourquet, Silvia Ronchetti, Daniele Mazza, In search of the cubic phase of the  $\text{Li}^+$  ion-conducting perovskite  $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$ : structure and properties of quenched and in situ heated samples, *Solid State Ionics* 149, (2002), 217-226.
- [13] Yoshiyuki Inaguma, Tetsuhiro Katsumata, Mitsuru Itoh, Yukio Morii, Takao Tsurui, Structural investigations of migration pathways in lithium ion-conducting  $\text{La}_{2/3-x}\text{Li}_{3x}\text{TiO}_3$  perovskites, *Solid State Ionics* 177, (2006), 3037-3044
- [14] Odile Bohnke, Joel Emery, Jean-Louis Fourquet, Anomalies in  $\text{Li}^+$  ion dynamics observed by impedance spectroscopy and  $^7\text{Li}$  NMR in the perovskite fast ion conductor  $(\text{Li}_{3x}\text{La}_{2/3-x}\text{TiO}_3)$ , *Solid State Ionics* 158 (2003) 119-132
- [15] T. Brousse, P. Fragnaud, R. Marchand, D. M. Schleich, O. Bohnke and K. West, All oxide solid-state lithium-ion cells, *Journal of Power Sources* 68, (1997), 412-415.

- [16] J. K. Ahn and S. G. Yoon, Characteristics of Amorphous Lithium Lanthanum Titanate Electrolyte Thin Films Grown by PLD for Use in Rechargeable Lithium Microbatteries, *Electrochemical and Solid State Letters* 8, (2005), A75-A78.
- [17] M. Morales, P. Laffez, D. Chateigner and I. Vickridge, Characterization of lanthanum lithium titanate thin films deposited by radio frequency sputtering on [100]-oriented MgO substrates, *Thin Solid Films* 418 (2002), 119-128.
- [18] D. L. Rousseau, R. P. Bauman S. P. S. Porto, Normal mode determination in crystal, *Journal of Spectroscopy*, vol. 10, (1981), 253-290.
- [19] M. L. Sanjuán and M. A. Laguna, Raman study of antiferroelectric instability in  $\text{La}_{(2-x)/3}\text{Li}_x\text{TiO}_3$  ( $0.1 < x < 0.5$ ) double perovskites *Phys. Rev. B* 64, 174305 2001
- [20] M. A. Laguna, M. L. Sanjuán, A. Várez, and J. Sanz, Lithium dynamics and disorder effects in the Raman spectrum of  $\text{La}_{(2-x)/3}\text{Li}_x\text{TiO}_3$ , *PHYSICAL REVIEW B* 66, (2002) 054301-1 - 054301-7
- [21] B. Sitamtze Youmbi, Serge Zékeng, Samuel Domngang, Florent Calvayrac, Alain Bulou, An ab initio molecular dynamics study of ionic conductivity in hexagonal lithium lanthanum titanate oxide  $\text{La}_{0.5}\text{Li}_{0.5}\text{TiO}_3$ , *Ionics* 18 (4), (2012), 371-377
- [22] O. Bohnke, C. Bohnke, J.L. Fourquet, Mechanism of ionic conduction and electrochemical intercalation of lithium into the perovskite lanthanum lithium titanate, *Solid State Ionics* 91 (1996) 21-31.

IJERT