

## Raman Characterization of LiNbO<sub>3</sub> Nanofibers Doped with Mn

MC Maldonado-Orozco<sup>1\*</sup>, R Narro-García<sup>1</sup>, CG Nava-Dino<sup>1</sup>, JP Flores-De los Ríos<sup>1</sup>, MT Ochoa-Lara<sup>2</sup> and F Espinosa-Magaña<sup>2</sup>

<sup>1</sup> Facultad de Ingeniería de la Universidad Autónoma de Chihuahua, Nuevo Campus s/n, Chihuahua, Chih. México.

<sup>2</sup> Centro de Investigación de Materiales Avanzados, S.C., Laboratorio Nacional de Nanotecnología. Miguel de Cervantes 120, Complejo Industrial, Chihuahua, Chih., México.

\* Corresponding author: cmaldona@uach.mx

The role that nanometric structures have played in science and technology has been a determining factor in the research that is currently being carried out around the world. Recently, it has been demonstrated, both theoretically and experimentally, that ABO<sub>3</sub> ferroelectric materials (A = K, Li, B = Ta, Nb or A = Ba, Sr, Pb, B = Ti) become multiferroic when they are brought to nanometric size, auguring a great advance in the optics and electronics of the future [1].

There are several methods that have been used for the synthesis of different nanostructures; specifically, in this work we concentrated on synthesizing pure lithium niobate nanofibers and doped with Mn, the manufacturing method was through electrospinning, the detailed explanation is found in reference [2]. This technique has been recognized as an efficient method to make polymeric nanofibers [3], who it is a straightforward way to synthesize nanostructures.

Through the electrospinning technique, the synthesis of lithium niobate necklace type nanofibers was performed. The morphology, microstructure and crystalline structure were characterized through Scanning Electron Microscopy (SEM), X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM) and Raman spectroscopy, ab initio calculations were also performed within the framework of the Dejection Functional Theory (DFT) within the Vienna Ab initio Simulation Package (VASP) and within the increased Projector Augmented Wave (PAW). In this work we will only discuss the results obtained in Raman spectroscopy and ab-initio calculations.

The phonons at point  $\Gamma$  are classified according to the irreducible representation of the point group  $C_{3v}$  and the group theory predicts the presence of the modes:  $4A_1 + 5A_2 + 9E$ . Modes  $A_1$  and  $E$  are Raman active modes, while  $A_2$  modes are not, see Fig 1.

Talking about ab-initio results, the  $A_1$  mode, calculated at  $253\text{ cm}^{-1}$  corresponds, according to the associated eigenvector, to an out-of-phase vibration of the Li and Nb ions along the z-axis, while the ions of O remain practically at rest. This mode is found in  $240$  and  $238\text{ cm}^{-1}$  in pure and doped nanofibers, respectively. The shift towards lower frequencies in the doped structure can be associated with the incorporation of Mn in the Li sites, since the mass of Mn is greater than that of Li.

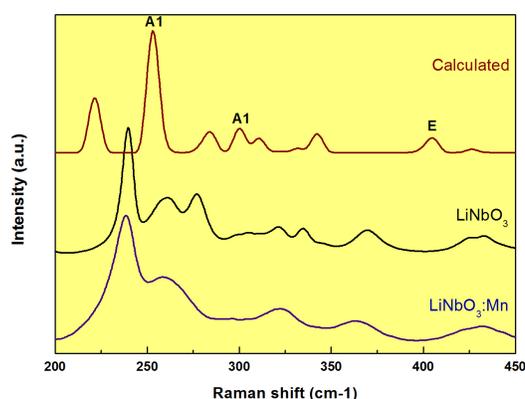
On the other hand, the  $E$  mode calculated at  $309.4\text{ cm}^{-1}$  comes from the vibrations of Nb, moving out of phase with its respective octahedron formed by the oxygen atoms, while the Li atoms remain practically at rest. This mode corresponds to frequencies of  $305\text{ cm}^{-1}$ , both in the pure structure and the doped one. This behavior indicates that there is no incorporation of Mn in the Nb sites. Finally, the  $E$  mode calculated at  $406\text{ cm}^{-1}$ , which in the two structures is at  $427\text{ cm}^{-1}$ , is due to the vibration of the oxygen

atoms only, which allows us to deduce that the Mn does not occupy O-sites either. these results can be seen in Table 1.

In summary, we can conclude that, at least for this concentration of doping, the Mn ions substitute only Li ions.

#### References:

- [1] S Sharma, *Adv. Mater. Lett.* **4** (2013), p. 522.  
 [2] MC Maldonado-Orozco et al., *Ceramics International* **41** (2015), p. 14886.  
 [3] H Byul Kang et al., *Appl. Mater. Interfaces* **6** (2014), p. 10576.



**Figure 1.** Raman spectra of LiNbO<sub>3</sub> nanofibers, pure and doped with Mn.

LiNbO <sub>3</sub>	LiNbO <sub>3</sub> :Mn (cm <sup>-1</sup> )	Calculated (cm <sup>-1</sup> )	Mode
240	238	253.0	A1 (TO)
305	305	310.8	A1 (TO)
427	427	404.8	E (TO)

**Table 1.** Measurements of frequencies (cm<sup>-1</sup>) of pure and doped LiNbO<sub>3</sub> and comparison with the frequency mode at point  $\Gamma$ , together with the irreducible representations.