

Raman Characterization of LiNbO₃ Nanofibers Doped with Mn

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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 ABO₃ 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 Density 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 Γ 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 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 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 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 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 cm^{-1} , which in the two structures is at 427 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.
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 [3] H Byul Kang et al., *Appl. Mater. Interfaces* **6** (2014), p. 10576.

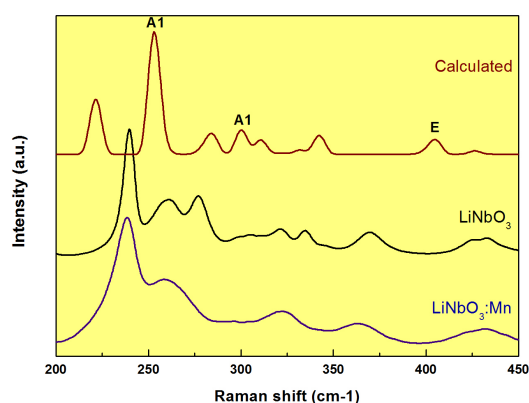


Figure 1. Raman spectra of LiNbO₃ nanofibers, pure and doped with Mn.

LiNbO ₃	LiNbO ₃ :Mn (cm ⁻¹)	Calculated (cm ⁻¹)	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⁻¹) of pure and doped LiNbO₃ and comparison with the frequency mode at point Γ , together with the irreducible representations.