

Study of Electronic Structure of LiNbO₃ Nanoparticles by EELS

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Lithium Niobate (LN) is one of the most intensively and exploited materials in fundamental and applied optics. Lithium Niobate is a ferroelectric material that exhibits spontaneous electric polarization that can be switched to its symmetry equivalent states with applied electric field. It is known that ferroelectricity is suppressed at the nano-scale, due to depolarization fields arising from the bound charges at the surface. For example, ferroelectricity in BaTiO₃ nanoparticles disappears below a critical size (40 nm). On the other hand, recent works have shown that ferromagnetism occurs in nanoparticles of the otherwise non-magnetic oxides, but decreases with increasing particle size. Magnetism in these nanoparticles, considered to arise from vacancies at the surface, is suggested to be a universal phenomenon. A recent finding of ferroelectricity in much smaller (12 nm) nanoparticles of BaTiO₃ motivated us to explore the simultaneous occurrence of ferromagnetism and ferroelectricity in nanocrystalline LiNbO₃. The dielectric properties of nanostructured LiNbO₃ are studied by analyzing the low-loss region of the electron energy loss spectroscopy (EELS) in a transmission electron microscope.

The electronic structure of LiNbO₃ nanoparticles has been studied by low-loss transmission electron energy loss spectroscopy in the shell region (1) and core region (2) as are shown in the Fig.1. Analyzing Figures 2 and 3 were found differences in both shape and energy position of peak in the energy loss function $\text{Im}[-1/\epsilon]$ from EELS. Shell spectra (Fig.2) a well-defined maximum around 11.17 eV can be attributed to a bulk-plasmon loss and the other less intense features to interband transition (6.13eV). Figure 3 shows EELS spectra a bulk plasmon in 14.55 eV and other peaks in 4.06, 8.7 eV. The excitations of valence electrons are dominated by collective excitations (plasmon) and the single interband transitions.

Table 1 shows the values of plasmon position (E_p) and the electronic density for LiNbO₃ regions. We calculated the electronic density, where we have observed the decrease of electronic density in the shell region of LiNbO₃. From these results it is evident the oxygen vacancies at the surface of the nanostructures. EELS analysis has been carried out for a better understanding of the electronic structure of core-shell nanoparticles. Changes in the electronic density (Shell) are due to oxygen vacancies at the surface of the nanostructures.

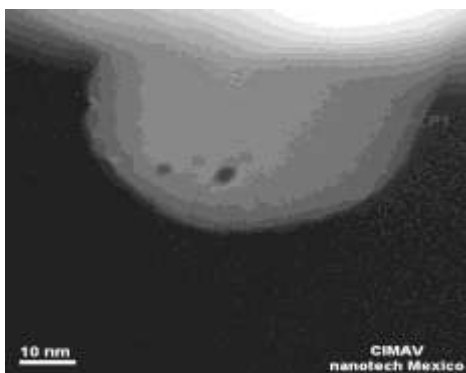


Figure 1. Micrograph of Nanostructure LiNbO₃

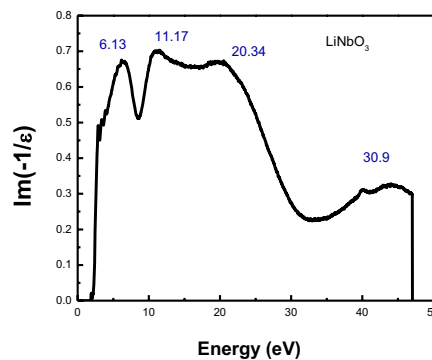


Figure 2. The energy loss function of Nanostructure LiNbO₃ (Shell).

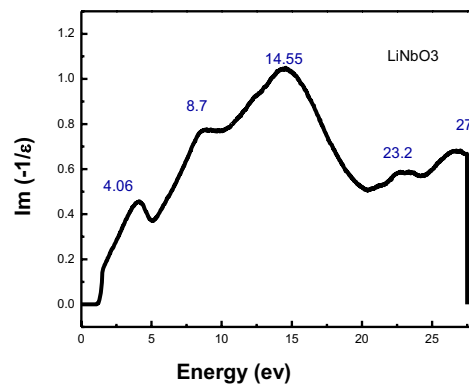


Figure 3. The energy loss function of LiNbO₃ Nanostructure (Core)

Table 1 Electronic density

Region	E _{max}	ΔE _p (eV)	E _p	Electronic density n _{3²⁹} (electron/m X10 ²⁹)
Shell	11.17	15.45	13.58	1.33
Core	14.55	11.97	15.68	1.79