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Study of Electronic Structure of $LiNbO_3$ 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 $BaTiO_3$ 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 $BaTiO_3$ motivated us to explore the simultaneous occurrence of ferromagnetism and ferroelectricity in nanocrystalline $LiNbO_3$. The dielectric properties of nanostructured $LiNbO_3$ are studied by analyzing the low-loss region of the electron energy loss spectroscopy (EELS) in a transmission electron microscope.

The electronic structure of $LiNbO_3$ 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 $Im[-1/\varepsilon]$ 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 (Ep) and the electronic density for $LiNbO_3$ regions. We calculated the electronic density, where we have observed the decresase 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.

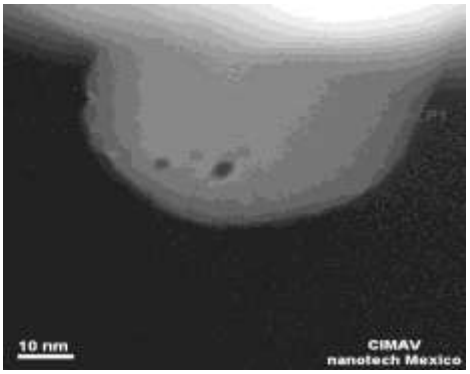

Figure 1. Micrograph of Nanostructure $LiNbO_3$

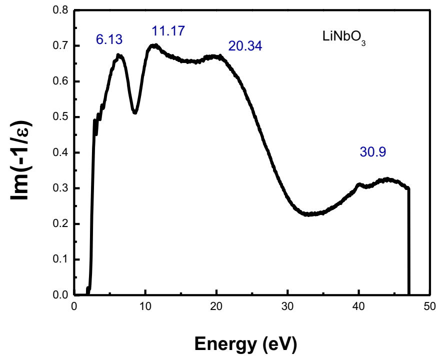

Figure 2. The energy loss function of Nanostructure $LiNbO_3$ (Shell).

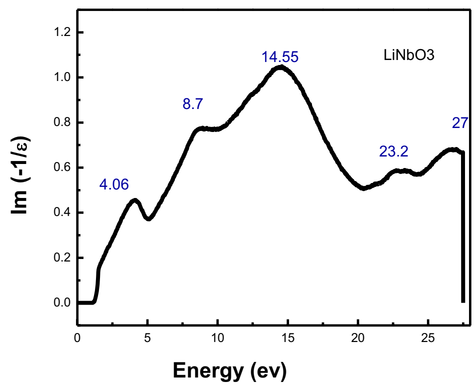

Figure 3. The energy loss function of LiNb03 Nanostructure (Core)

Table1 Electronic density

Region	Emax	ΔEp (eV)	Ep	Electronic density n (electron/m^3 X10^{29})
Shell	11.17	15.45	13.58	1.33
Core	14.55	11.97	15.68	1.79