

## A Study of the $LiNbO_3$ and $LiTaO_3$ Absorption Edge

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### Abstract

Optical spectroscopy methods are used to study the spectra of some oxygen-octahedral ferroelectrics -  $LiNbO_3$  and  $LiTaO_3$ . Study of the role of  $BO_6$  octahedron by using spectroscopic methods can cast light on the many physical phenomena that place in  $LiNbO_3$  and  $LiTaO_3$ . For these crystals, absorption edge, band gap, Urbach constants and phonon energy were found.

### 1. Introduction

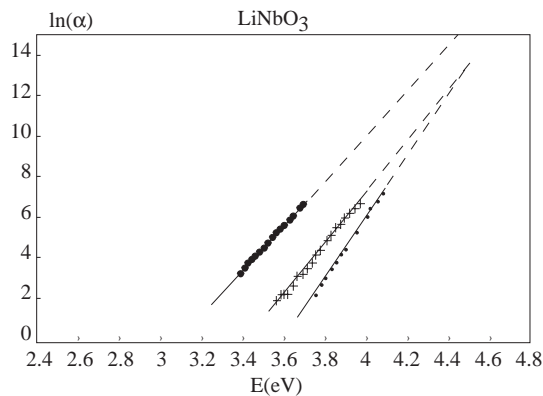
One of the most important and numerous of the groups of ferroelectrics is the family of oxygen-octahedron crystals which are the single crystals  $LiNbO_3$  and  $LiTaO_3$ , which have been studied intensively over the past 15 years. The great interest in these crystals is due to their strong optical nonlinearity and electro-optic effect. The interest in these compounds, however, is not restricted to application only. The presence of the  $BO_6$  octahedron with different  $B - O$  bonds in  $LiNbO_3$  and  $LiTaO_3$  and the displacement of the  $B$  ion in the octahedron for the different basic structures lead to changes in many of the macroscopic and microscopic parameters of these crystals [1-2].

This work is directed towards the study of the optical properties of  $LiNbO_3$  and  $LiTaO_3$  over the temperature range  $T = 100 - 400K$  and in the region of fundamental absorption ( $\hbar\omega = 3-4.6$  eV) for the purpose of discovering the features of the electron energy spectrum and determining the role of the  $BO_6$  octahedral in the formation of the band structure of these compounds.

## 2. Absorption Edge Studies

The  $\alpha$  absorption factor in the substance was calculated by measuring the transmission factor and the reflection factor and then inserting these measured numbers into the well-known formula. [3]

We shall report one of the first detail investigations of absorption edge of oxygen-octahedral ferroelectrics -  $LiNbO_3$  and  $LiTaO_3$ . We investigated the  $\alpha$  spectral dependence for three temperature levels: 200 K, 300 K and 373 K (Fig. 1). It is clear from Figure 1 that absorption factor varies exponentially with the falling photon energy following the Urbach law: [3]



**Figure 1.** The spectral dependences of absorption coefficient for  $LiNbO_3$ , ( $\cdot$ ) : 200K, ( $\times$ ) : 300K, ( $*$ ) : 373K .

$$\alpha = \alpha_0 \exp \left[ \frac{\sigma}{kT^*} (hv - E_0) \right] \quad (1)$$

where  $\sigma$  is the characteristic constant,  $\alpha_0$  is the extreme values of  $\alpha$ ,  $E_0$  is the forbidden band energy with corresponding to  $\alpha_0$  and  $T^*$  is the effective temperature being determined from [3]

$$T^* = \frac{\hbar\omega_p}{2k} \coth \left( \frac{\hbar\omega_p}{2kT} \right), \quad (2)$$

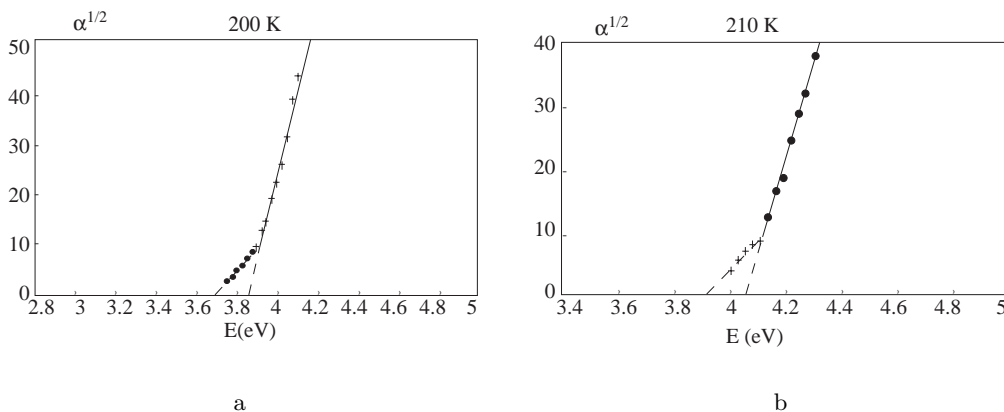
where  $T$  is the absolute temperature, and  $\omega_p$  is the phonon frequency at which the most active interaction occurs with electrons.

The absorption edge steepness is identical for both light polarizations and at different temperature amounts to a value of  $S (= \frac{\sigma}{kT^*})$ .  $S$  values reasonably corresponds to the  $LiNbO_3$  and  $LiTaO_3$  absorption edge steepness calculated. The frequency of the phonons involved in the absorption process was calculated graphically by the  $S$  steepness for three temperatures. This was done through formula (2) and resulted in a  $\omega_p$  and  $\sigma$ . For decreasing temperature the optical absorption edge inclination increases

as  $S \sim 1/(T + T_0)$ , where  $T_0$  is a characteristic temperature with the  $kT_0$  value for all measured temperatures remains approximately constant. By using the Toyozawa model [3] we calculated the energy (Table 1) and thus the type of effective phonons. The results obtained from our absorption data agrees well with the  $\omega_p$  obtained from Raman and IR spectra of  $ABO_3$  crystals [4-6]. The effective phonons energy obtained from our absorption data for  $LiTaO_3$  were bigger than  $LiNbO_3$  and other ferroelectric semiconductors. These crystals have strong electron-phonon interaction and low energy electrons are excited from valence band to conduction band aiding phonons.

Extrapolation of  $\alpha$  for absorption values yielded  $\alpha_0$  and  $E_0$  values (for  $LiNbO_3$ ,  $\alpha_0 = 6.65 \times 10^5 1/cm$ ,  $E_0 = 4.502eV$ ; for  $LiTaO_3$   $\alpha_0 = 1.47 \times 10^4 1/cm$ ,  $E_0 = 4.44eV$ ). Using the same absorption values the isoabsorption curves were formed and calculated  $E_0$  (for  $LiNbO_3$ ,  $E_0 = 4.2eV$ ; and for  $LiTaO_3$ ,  $E_0 = 4.2eV$ ).

With reduced temperature the absorption edge shifts towards greater energies with the average temperature factor of  $dE_g/dT$  (for  $LiNbO_3$   $dE_g/dT = -2.745 \times 10^{-3} eV/K$ ; for  $LiTaO_3$   $dE_g/dT = -5.52 \times 10^{-4} eV/K$ ). For decreasing temperature the optical absorption edge inclination increases as  $\sim 1/T$ .



**Figure 2.** The energy dependence of  $\alpha^{1/2}$ , (a)  $LiNbO_3$ , (b)  $LiTaO_3$ .

Below 240 K and in high energy region absorption edges becomes abrupt and indirect optical transitions from phonon participation are observed in experiment. The spectral dependences of  $\alpha$  are illustrated in Fig. 2a, b, where the square root of  $\alpha$  is plotted to yield a linear dependence on  $h\nu$ . Such a plot, by extrapolation to  $\alpha = 0$ , gives the values of  $E_g - E_p$  and  $E_g + E_p$ . Measurement results for  $LiNbO_3$  and  $LiTaO_3$  are given in Table 1. Note that  $E_g$  has been shifted with temperature to reflect the temperature dependence of the energy gap.

**Table 1.** Band gap, phonons and effective phonons energy values

Crystal	$T(K)$	$E_g(eV)$	$E_p(eV)$	$E_p^*(eV)$
<i>LiNbO<sub>3</sub></i>	200	3.780	0.0800	0.0857
	300	3.635	0.085	0.0999
	373	3.305	0.095	0.109
<i>LiTaO<sub>3</sub></i>	210	3.985	0.075	0.208
	300	3.930	0.09	0.274
	373	3.895	0.06	0.321

### 3. Discussion

The optical properties of *LiNbO<sub>3</sub>* and *LiTaO<sub>3</sub>* single crystals have been investigated in the energy region 3-4.6 eV. Indirect optical transitions are observed experimentally. The width of the forbidden band gap  $E_g$  for indirect optical transitions is determined on the basis of the spectral dependence of  $\alpha^{1/2}$  (absorption coefficient). We examined electron-phonon interaction and noted the forbidden band gap varying with temperature.

However, the known theoretical calculations of *SrTiO<sub>3</sub>* band structure [7] are based on the principle role of the  $BO_6$  octahedron. Taking into account that *LiNbO<sub>3</sub>* and *LiTaO<sub>3</sub>* involve  $BO_6$  octahedrons as well, let us try to compare our experimental data with the known theoretical calculations [7]. The comparison allows us to state that the principal peculiarities of *SrTiO<sub>3</sub>* band structure are preserved both for *LiNbO<sub>3</sub>* and *LiTaO<sub>3</sub>*. But certainly, there are some changes due to the  $Nb^{5+}(d)$ ,  $Li^+(2s)$  and  $Ta^{5+}(d)$  wave functions.

The similarity of optical functions for *LiNbO<sub>3</sub>* and *LiTaO<sub>3</sub>* within the  $\hbar\omega = 3 - 4.6 eV$  range indicates the  $BO_6$  octahedron fundamental significance in the band structure formation. It means that the  $BO_6$  octahedron determines the lowest boundary of the conduction band and the upper boundary of the valence band. Oxygen electron levels (2p) form *LiNbO<sub>3</sub>* and *LiTaO<sub>3</sub>* valence band, while the conduction band of these crystals is formed by the *Nb* and *Ta* d-orbitals.

### 4. Conclusion

*LiNbO<sub>3</sub>* and *LiTaO<sub>3</sub>* optical properties have been studied within  $\hbar\omega = 3 - 4.6 eV$ . Optical function have been calculated. The  $BO_6$  octahedron role in the formation of *LiNbO<sub>3</sub>* and *LiTaO<sub>3</sub>* band structure have been revealed.

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