Turkish Journal of Physics

Volume 22 | Number 1 Article 5

1-1-1998

A Study of the LiNbO_3 and LiTaO_3 Absorption Edge

S. ÇABUK

A. MAMEDOV

Tr. J. of Physics
22 (1998) , 41 – 45.

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

Süleyman ÇABUK, Amirullah MAMEDOV
Department of Physics,
Faculty of Arts and Sciences,
Çukurova University,
01330 Adana-TURKEY

Received 3.09.1996

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 α 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 α 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]

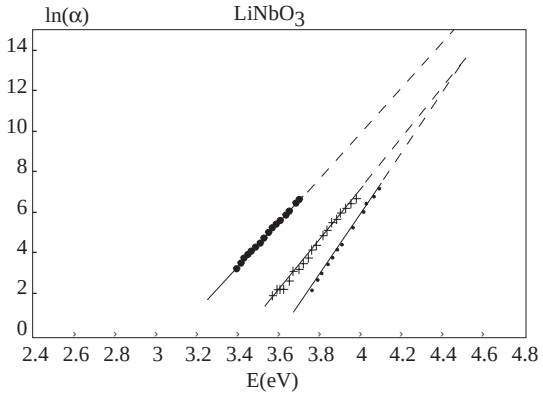


Figure 1. The spectral dependences of absorption coefficient for $LiNbO_3$, $(\cdot) : 200K, (x) : 300K, (*) : 373K$.

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

where σ is the characteristic constant, α_0 is the extreme values of α, E_0 is the forbidden band energy with corresponding to α_0 and T^* is the effective temperature being determined from [3]

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

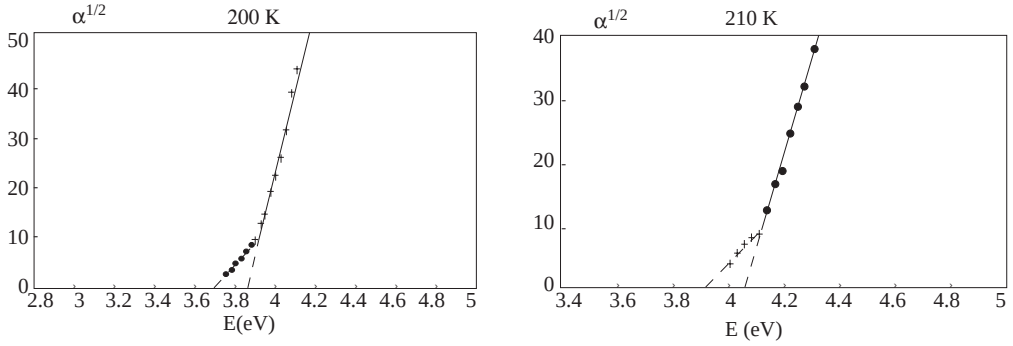
where T is the absolute temperature, and ω_p is the phonon frequency at which the most active interaction occurs with electrons.

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 ω_p and σ. 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 ω_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 α for absorption values yielded α_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 $\sim 1/T$.



a b

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 α are illustrated in Fig. 2a, b, where the square root of α is plotted to yield a linear dependence on hv. 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	$T(K)$	$E_g(eV)$	$E_p(eV)$	$E_p^*(eV)$
$LiNbO_3$	200	3.780	0.0800	0.0857
	300	3.635	0.085	0.0999
	373	3.305	0.095	0.109
$LiTaO_3$	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 $LiNbO_3$ and $LiTaO_3$ 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 $SrTiO_3$ band structure [7] are based on the principle role of the BO_6 octahedron. Taking into account that $LiNbO_3$ and $LiTaO_3$ 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 pecularities of $SrTiO_3$ band structure are preserved both for $LiNbO_3$ and $LiTaO_3$. 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 $LiNbO_3$ and $LiTaO_3$ 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 $LiNbO_3$ and $LiTaO_3$ valence band, while the conduction band of these crystals is formed by the Nb and Ta d-orbitals.

4. Conclusion

$LiNbO_3$ and $LiTaO_3$ 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 $LiNbO_3$ and $LiTaO_3$ band structure have been revealed.

References

[1] G.E. Jellison, L.A. Boather, D.H. Lowndes, R.A. McKee, M. Godbole, Appl. Optics, **33** N25 (1994) 6053-6055.

[2] K. Benaissa, P.V. Ashrit, G. Bader, Vo-Van Truong, Thin Solid Films, **24** (1992) 219-222.

[3] M.E. Lines and A.M., Glass Principles and Applications of Ferroelectrics and Related Materials (Clarendon Press, Oxford) (1977) 420.

[4] R. Blinc and B. Zeks, Soft Modes in Ferroelectrics and Antiferroelectrics, NHP (1974).

[5] E.W. Kellermann, Model for Longwave Length Optical Phonon Modes in Mixed Crysals, Phil. Trans. Rey. Soc., **A238** (1980) 513.

[6] T. Wolfram, Phys. Rev., **119** (1969) 980.

[7] A.H. Kahn, A.J. Leyendecker, Phys. Rev., **135** A1321 (1964).