Results in Physics 39 (2022) 105736

Contents lists available at ScienceDirect

Results in Physics

journal homepage: www.elsevier.com/locate/rinp

Microarticle

The optical bandgap of lithium niobate ($LiNbO_3$) and its dependence with temperature

A.R. Zanatta

Instituto de Física de São Carlos, USP, São Carlos 13560-970, SP, Brazil

ARTICLE INFO

Keywords:
Lithium niobate ($LiNbO_3$)
Optical spectroscopy
Optical bandgap
Photonic devices

ABSTRACT

Notwithstanding the great scientific−technological interest in lithium niobate ($LiNbO_3$), its optical bandgap E_{gap} has been subject of intense discussion. So far, the literature exhibits different E_{gap} values spanning over about 2 eV and comprises a mixture of compositions, structures, and theoretical methods − not always clearly indicated or discussed. In view of that, this work presents a thorough investigation of the E_{gap} (at room-temperature and in the ~80–800 K temperature range) of the congruent ferroelectric $LiNbO_3$ (Z-cut) single crystal.

Lithium niobate ($LiNbO_3$) is a manmade material that, since its advent, has fascinated the scientific community because of its non-linear, electro-optical, and photo-refractive outstanding properties [1]. As a consequence, $LiNbO_3$ is considered the *"Silicon of Photonics"* with practical applications ranging from wavelength (or surface acoustic wave) filters to optical waveguides (or modulators) and optical frequency converters (or oscillators) − just to mention a few of them [2]. In most of these applications, crystalline $LiNbO_3$ wafers are prepared by *Czochralski* − in which the X-, Y-, or Z-cuts indicate the crystallographic axes that are normal to the large wafer surfaces − and exhibit a non-stoichiometric composition (typically 48.5 ± 0.5 mol% of Li_2O), rendering a Li-deficient structure and lots of defects [1,3]. Contrasting with these so-called congruent $LiNbO_3$, better quality stoichiometric $LiNbO_3$ can be achieved, though at higher costs. In terms of properties, it is common sense that, below its *Curie* temperature Θ_{Curie} (~1420 K), $LiNbO_3$ is ferroelectric (space group $R3c$) consisting of oxygen octahedra sharing faces along the 3-fold axis [1]. Paraelectric $LiNbO_3$ (space group $R\bar{3}c$) is stable only above Θ_{Curie} and, therefore, has received comparatively less attention than its ferroelectric phase. Notwithstanding such scientific interest and its many successful technological achievements, the optical bandgap E_{gap} of $LiNbO_3$ is still under debate. This seems somewhat contradictory given the importance of the E_{gap} (value and behavior) in developing practical devices but, at present, the literature regarding the E_{gap} of $LiNbO_3$ is rather diffuse. Just to illustrate the point, it is usual to find experimental E_{gap} values in the 3.3–4.7 eV [4−[7]] range, along with those provided by theoretical figures ranging from 3.5 to 6.5 eV [8]. Whereas most of the discrepancies in the experimental E_{gap} values arise because of differences in the composition and structure of $LiNbO_3$ (*i.e.*: congruent *vs* stoichiometric, ferroelectric *vs* paraelectric, pure *vs* doped materials, etc.), the theory behind E_{gap} seems to be highly influenced by the calculation methods − inputs as well. Another issue is related to the nature of the optical transitions in $LiNbO_3$ − most likely indirect [4,5] (in spite of some misleading citations [8]).

The above scenario form the basis of this work that investigates the optical bandgap E_{gap} of congruent $LiNbO_3$, as determined by optical transmission measurements as a function of temperature. In fact, in contrast to the only existing temperature-dependent E_{gap} report on $LiNbO_3$ [9], this paper presents a detailed compositional − structural analysis of the $LiNbO_3$ crystal as well as a comprehensive analysis of E_{gap} according to standard procedures.

The sample considered in this work corresponds to a commercial (congruent, ferroelectric, undoped, optical grade, Z-cut, 2-side polished) $LiNbO_3$ single crystal. Both the atom structure and composition of the sample was verified by Raman spectroscopy (backscattering geometry, 632.8 nm excitation). Optical transmittance ($\mathcal{T}$) and reflectance ($\mathcal{R}$) measurements were carried out in the ~250–1000 nm range by means of a miniature spectrophotometer, optical fibers, and integrating sphere. All spectra were properly corrected by the optical response of the system (light source + diffraction grating + detector) to ensure 100% light transmission or reflection (from a Al mirror reflectance standard). Additional $\mathcal{T}$ measurements were performed in the 83–773 K temperature range (in steps of either 25 or 50 K) with the sample placed in a temperature-stage. In this case, a dwell time of 3 min was adopted before each measurement to allow the sample to reach thermal equilibrium.

A typical Raman spectrum of the $LiNbO_3$ single crystal, taken in the $z(x,xy)\bar{z}$ orientation, is shown in Fig. 1(a). Exactly the same spectrum was achieved by imposing different laser and/or detection polarization conditions (and after sample rotation), confirming that the crystal corresponds to the Z-cut [10].

In addition to the crystal quality and orientation, the Raman spectrum was considered to assess the $LiNbO_3$ composition. The estimate is based on the fact that any change in the $LiNbO_3$ crystal lattice (*i.e.*:

https://doi.org/10.1016/j.rinp.2022.105736
Received 26 April 2022; Received in revised form 31 May 2022; Accepted 11 June 2022
Available online 14 June 2022
2211-3797/© 2022 The Author. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

translational symmetry, atoms masses, and force constants) influences its internal potential. As a result, in non-stoichiometric $LiNbO_3$, the substitution of Li by Nb atoms modifies the overall phonon behavior increasing the linewidth (FWHM) of certain phonon modes. The concept was originally proposed by *Schlarb et al.* and, since then, it has been used to infer the relative amount of Li_2O in $LiNbO_3$ crystals – simply by applying the experimentally determined linewidths of the E(TO1) and/or A1(LO4) modes into some calibration curves [11]. Fig. 1(b) and 1(c) show the *Lorentzian* curve fittings of these modes, according to which the average [Li_2O] was found to be 48.5 ± 0.3 mol%.

Fig. 1(e) shows the optical absorption coefficient α(E) – as obtained from the room-temperature $\mathcal{T}$ and $\mathcal{R}$ spectra of Fig. 1(d) – along with the sigmoid-*Boltzmann* curve that best reproduces the α(E) data. According to this procedure the optical bandgap is given by $E_{gap}^{Boltz} = E_0^{Boltz} - n_{type}^{Boltz} \cdot \delta E$, where E_0^{Boltz} and δE correspond to the central energy and slope of the sigmoid-*Boltzmann* function, and the empirical n_{type}^{Boltz} parameter stands for the type of optical transition or bandgap ($n_{direct}^{Boltz} = 0.3$ and $n_{indirect}^{Boltz} = 4.3$) [12]. Given its simplicity, insensitivity to measurements–analyses problems, and E_{gap} uncertainties comparable to (or below) those exhibited by other methods, the *Boltzmann*-related method was adopted in this work. Accordingly, an indirect $E_{gap}^{Boltz} = 3.77 \pm 0.05$ eV has been achieved for congruent (Z-cut) $LiNbO_3$, at room-temperature.

Because of experimental restrictions, only the transmittance $\mathcal{T}$ of $LiNbO_3$ was measured as a function of temperature – a few α(E) spectra, as derived from these $\mathcal{T}$ measurements, are displayed in Fig. 1(f). As can be seen, the spectra experience a clear red-shift at increasing temperatures. This temperature-induced effect can be evaluated, for example, by representing the E_{gap} of $LiNbO_3$ as a function of temperature $E_{gap}(T)$ – as shown in Fig. 2. The figure also indicates the $E_{gap}(T)$ values of *Redfield & Burke* [9], as well as the E_{gap} at room-temperature of some other references. In addition to the $E_{gap}(T)$ behavior, it is impressive the data dispersion at room-temperature. According to Fig. 2, the room-temperature E_{gap} of congruent $LiNbO_3$ occurs predominantly at ~ 3.8 eV, even though certain E_{gap} values at 3.3 eV and 4.7 eV – this time, however, regarding materials with unknown composition [6] and/or no clear atomic structure [7]. Besides, the $E_{gap}(T)$ of reference 9 corresponds to a mix of congruent $LiNbO_3$ crystals of different orientations and thicknesses and, particularly, by supposing E_{gap} as the energy at which $\alpha = 2000\ cm^{-1}$.

Taking into account this variety of values–conditions–methods

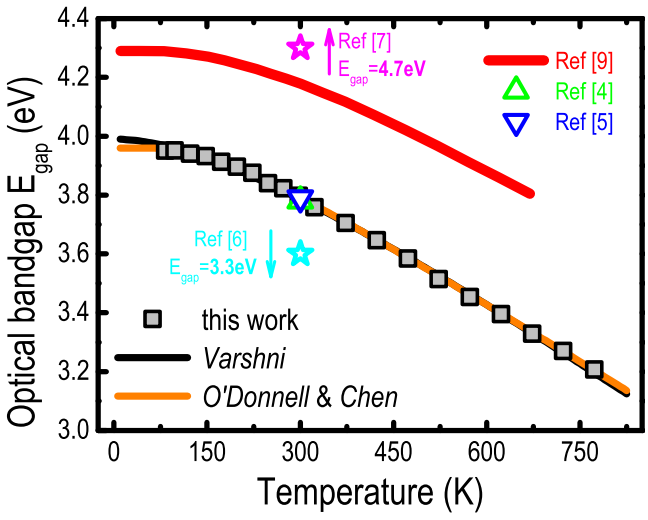

Fig. 2. Optical bandgap E_{gap} of a $LiNbO_3$ crystal (congruent, Z-cut) as a function of temperature – as obtained in this work, along with some theoretical expressions (by *Varshni* [13] and *O'Donnell & Chen* [15]) – as well as some data from literature.

from literature, the experimental results obtained in the present work (based on a well-characterized crystal and following standard procedures) were considered to explore the temperature-dependent E_{gap} behavior of $LiNbO_3$. In fact, both E_{gap} and $E_{gap}(T)$ are fingerprints of many materials and knowing their values and behavior are essential to produce new–improved semiconductor-related devices. Traditionally, the study of $E_{gap}(T)$ involves the analysis of the experimental data according to the empirical description by *Varshni* [13], such that $E_{gap}(T) = E_{gap}(0) - \frac{P_1 T^2}{P_2 + T}$, where $E_{gap}(0)$ stands for the E_{gap} at T = 0 K, and P_1 and P_2 are fitting parameters (characteristic of each material). Further studies consider the separation of $E_{gap}(T)$ into contributions: due to lattice expansion/contraction effects and electron–phonon interactions [14]. Although most of these approaches reproduce the experimental $E_{gap}(T)$ with some precision, unfortunately, not all of them are straightforward and/or provide realistic physical information. An alternative way to overcome part of these problems – still involving an empirical treatment, but based on simple thermodynamic concepts – was proposed by *O'Donnell & Chen* [15]. Roughly, the model takes into consideration the

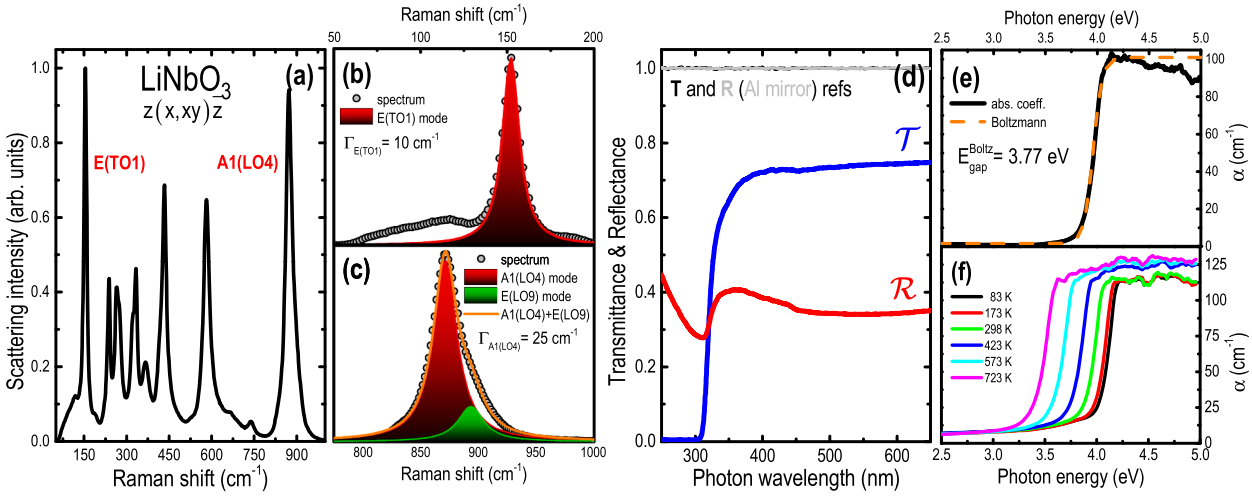

Fig. 1. (a) Room-temperature Raman scattering spectra ($z(x,xy)\bar{z}$ orientation) of a $LiNbO_3$ single crystal (Z-cut). (b) Detail of the E(TO1) phonon mode and its corresponding *Lorentzian* curve fitting (FWHM = $\Gamma_{E(TO1)} = 10\ cm^{-1}$). (c) Detail of the A1(LO4) and E(LO9) phonon modes and corresponding curve fittings ($\Gamma_{A1(LO4)} = 25\ cm^{-1}$). (d) Optical transmittance $\mathcal{T}$ and reflectance $\mathcal{R}$ spectra of $LiNbO_3$. (e) Respective absorption coefficient α, at room-temperature, indicating an indirect $E_{gap}^{Boltz} = 3.77$ eV. (f) Absorption coefficient spectra (as obtained from $\mathcal{T}$) at various temperatures.

similar (average) temperature-dependent effect that crystal lattice and electron−phonon coupling have on E_{gap}, according to which the experimental data can be described by $E_{gap}(T) = E_{gap}(0) - S\langle\hbar\omega\rangle\left[\coth\left(\frac{\langle\hbar\omega\rangle}{2k_BT}\right) - 1\right]$, where $E_{gap}(0)$ is the bandgap value at T = 0 K, S is a dimensionless coupling constant, and $\langle\hbar\omega\rangle$ is an average phonon energy. The theoretical analysis of the present E_{gap}(T) data is shown in Fig. 2, according to which it is clear the differences between the models by *Varshni* and *O'Donnell & Chen* − in special at very low temperatures. Furthermore, the approach by *O'Donnell & Chen* perfectly fits the experimental E_{gap}(T) data in the whole 83–773 K temperature range providing quite reasonable values with $\hbar\omega \sim 40$ meV (*i.e.*, on the order of the typical phonon frequencies of $LiNbO_3$ − see Fig. 1(a)), and presenting E_{gap} values somehow stationary below T ∼ 50 K.

In summary, this work presents the first comprehensive study of the optical bandgap E_{gap} of the $LiNbO_3$ crystal (congruent, Z-cut). Accordingly, the indirect optical bandgap of $LiNbO_3$ was found to comply with $E_{gap}^{IND}(T) = 3.96 - 0.311\left[\coth\left(\frac{0.04}{2k_BT}\right) - 1\right]$, rendering $E_{gap}^{IND}(T) = 3.77 \pm 0.05$ eV at room-temperature.

Funding

This work was financially supported by the Brazilian agencies CNPq (Grant 304569/2021-6) and FAPESP.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] Weis RS, Gaylord TK. Lithium niobate: Summary of physical properties and crystal structure. Appl Phys A 1985;37(4):191–203.
[2] Wu L, Zhang Xi, Fu Yi, Xu Z, Ding X, Yao J. Tuning the dielectric properties of $LiNbO_3$ based interdigitated electrode metastructure in the terahertz range. Res Phys 2021;24:104120.
[3] Anikiev A, Umarov MF, Scott JF. Processing and characterization of improved congruent $LiNbO_3$. AIP Adv 2018;8:115016. https://doi.org/10.1063/1.5055386.
[4] Dhar A, Mansingh A. Optical properties of reduced lithium niobate single crystals. J Appl Phys 1990;68(11):5804–9.
[5] Bhatt R, Kar S, Bartwal KS, Wadhawan VK. The effect of Cr doping on optical and photoluminescence properties of $LiNbO_3$ crystals. Sol St Commun 2003;127(6):457–62.
[6] Jiangou Z, Shipin Z, Dingquan X, Xiu W, Guanfeng Xu. Optical absorption properties of doped lithium niobate crystals. J Phys: Condens Matter 1992;4(11):2977–83.
[7] Satapathy S, Mukherjee C, Shaktawat T, Gupta PK, Sathe VG. Blue shift of optical band-gap in $LiNbO_3$ thin films deposited by sol-gel technique. Thin Solid Films 2012;520(21):6510–4.
[8] Thierfelder C, Sanna S, Schindlmayr A, Schmidt WG. Do we know the band gap of lithium niobate? Phys Phys Status Solidi (c) 2010;7(2):362–5.
[9] Redfield D, Burke WJ. Optical absorption edge of $LiNbO_3$. J Appl Phys 1974;45(10):4566–71.
[10] Scott JG, Mailis S, Sones CL, Eason RW. A Raman study of single-crystal congruent lithium niobate following electric-field repoling. Appl Phys A 2004;79(3):691–6.
[11] Schlarb U, Klauer S, Wesselmann M, Betzler K, Whiilecke M. Determination of the Li/Nb ratio in lithium niobate by means of birefringence and Raman measurements. Appl Phys A 1993;56(4):311–5.
[12] Zanatta AR. Revisiting the optical bandgap of semiconductors and the proposal of a unified methodology to its determination. Sci Rep 2019;9:11225. https://doi.org/10.1038/s41598-019-47670-y.
[13] Varshni YP. Temperature dependence of the energy gap in semiconductors. Physica 1967;34(1):149–54.
[14] Cardona M, Kremer RK. Temperature dependence of the electronic gaps of semiconductors. Thin Solid Films 2014;571:680–3.
[15] O'Donnell KP, Chen X. Temperature dependence of semiconductor band gaps. Appl Phys Lett 1991;58(25):2924–6.