Electronic properties of lithium tantalate using Compton spectroscopy

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Abstract: We have measured the electron momentum density (EMD) of LiTaO$_3$ using 100 mCi $^{241}$Am Compton spectrometer. The experimental Compton profile (CP) is compared with theoretical EMDs deduced using linear combination of atomic orbitals (LCAO) method with different exchange and correlation potentials namely PBE, PWGGA and VBH. On the basis of $\chi^2$ fit (which scales goodness of fitting) and difference profiles between experimental and theoretical CPs, LCAO-PWGGA potential based CP is found close to experimental results. Electronic properties like energy bands and density of states of LiTaO$_3$ using LCAO-PWGGA potential show a band gap of 4.85 eV of LiTaO$_3$ thereby depicting its semiconductor nature with wide band gap. It is observed that upper valence band region is mainly dominated by 2p states of O and 5d states of Ta, although there is small contribution of 2s states of Li in this region.

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1. Introduction
Ferroelectric materials possess several applications in piezoelectric devices, waveguides, holography, photorefractive devices, nonlinear optical devices, etc. Ferroelectric materials like LiTaO$_3$ depict phase transition at 950 K from paraelectric to room temperature ferroelectric (R3c) phase and acquires higher spontaneous polarization [1-2]. He et al. [3] have reported formation energies of charged and neutral vacancies in LiTaO$_3$ by applying first-principles calculations.

Compton spectroscopy is a well-recognized and competent technique to validate the electronic structure of variety of materials [4-5]. Within the limitation of impulse approximation, the measured double differential Compton scattering cross-section is directly proportional to the Compton profile (CP), $J(p_z)$. Moreover, the $J(p_z)$ is projection of electron momentum density (EMD) along z-axis which is basically considered as the scattering vector direction [6]. Mathematically,

$$\frac{d^2\sigma}{d\Omega d\omega_2} \propto J(p_z) = \int \int n(p) dp_x dp_y,$$

(1)
where, \( n(\hat{p}) \) is the three dimensional EMD.

To throw more light on the electronic response of lithium tantalate, we report the experimental isotropic CP measured by \(^{241}\)Am Compton spectrometer and theoretical profiles derived using linear combination of atomic orbitals (LCAO) method with various exchange and correlation potentials like Perdew-Burke-Ernzerhof (PBE), Perdew-Wang generalized gradient approximation (PWGGA) and Von Barth-Hedin (VBH). In addition, we have also discussed Compton line shape in terms of energy bands (E-k relations) and density of states (DOS) of LiTaO\(_3\) using LCAO-PWGGGA approximation.

2. Methodology

2.1 Experiment

In the present Compton measurement, we have employed 100 mCi \(^{241}\)Am Compton spectrometer with overall instrumental resolution (Gaussian FWHM) of 0.55 a.u. [7]. A circular slab of polycrystalline sample (radius and thickness about 1.28 and 0.46 cm, respectively) was mounted vertically inside the scattering chamber. The \( \gamma \)-radiations with principal energy line of 59.54 keV were incident on the slab and the scattered \( \gamma \)-ray photons at 165±1.5° were analyzed by a high planar Ge detector (Canberra, Model GL0210P) and requisite standard electronics. To obtain the absolute CP, the measured raw data were corrected for well explored corrections like background, removal of low energy tail in the response of HPGe detector, absorption and scattering cross-section, multiple (up to triple) scattering, etc. [8]. In order to avoid residual instrumental resolution effect, the deconvolution correction was confined to stripping-off the low energy tail of Compton spectrum. Finally, the experimental profile was normalized (in the momentum range 0-7 a.u.) to the corresponding free atom profile area (38.90 e–) of LiTaO\(_3\) [9].

2.2 Theory

The theoretical CPs, electronic band structure and DOS were derived by employing PBE, PWGGA and VBH exchange and correlation potentials within LCAO method as facilitated in CRYSTAL14 package [10]. In the present calculations, the experimental lattice parameters of LiTaO\(_3\) have been taken as \( a=5.154 \) Å and \( c=13.783 \) Å [2]. The Gaussian-type basis sets of Li, Ta and O were taken from www.tcm.cam.ac.uk and all the basis sets have been optimized for lowest energy using BILLY program for LiTaO\(_3\) system leading to its stability [11]. Self-consistent computations were performed using 65 reciprocal (\( \mathbf{k} \)) points in the irreducible Brillouin zone (BZ) with convergence criteria of \( 10^{-6} \) Hartree.

3. Results and discussion

3.1 Compton profile

In Fig. 1, we have plotted the differences between isotropic experimental CP and convoluted theoretical CPs deduced using LCAO-PBE, -PWGGA and -VBH approximations. From Fig. 1, it is clearly observed that all the theoretical profiles show closeness to the experimental profile in the intermediate and high momentum region (\( pz > 3 \) a.u.) because of dominance of core electrons in this region. However, in the low momentum (valence electron) region, there are differences between the experimental and theoretical CPs which may be explained in terms of (a) performance of DFT theory (b) possibility of further improvement of Gaussian basis functions used in the LCAO calculations and (c) non-relativistic computation in LCAO scheme. We have attempted \( \chi^2 \) fitting to find out the most reliable exchange and correlation potentials for LiTaO\(_3\) among those considered in the present manuscript. \( \chi^2 \) function involves experimental and theoretical CPs and statistical errors (\( \pm \sigma \)) which is formulated as,
The values of $\chi^2$ for LCAO-PBE, -PWGGA and -VBH prescriptions were computed as 2030.78, 2022.76 and 2132.73, respectively. Therefore, we conclude that theoretical CP based on LCAO-PWGGa method is more consistent with experimental profile, as compared to other exchange and correlation potentials.

$$\chi^2 = \sum_{p_z=0}^{2} \left[ \frac{J^{th}(p_z) - J^{exp}(p_z)}{\sigma(p_z)} \right]^2$$

(2)

Figure. 1. Differences between experimental and convoluted theoretical profiles of LiTaO$_3$ derived using LCAO-PBE, -PWGGA and -VBH approaches.

3.2 Energy bands and DOS

E-k relations and DOS of LiTaO$_3$ within LCAO-PWGGa calculations are shown in Figures. 2. (a and b). The energy bands and DOS computed using LCAO-PBE and -VBH approximation show almost identical topology with those obtained using LCAO-PWGGa scheme. Since the maximum of valence band (VB) and minimum of conduction band (CB) lie at $\Gamma$ point of BZ, we find a direct band gap of 4.85 eV of the LiTaO$_3$. Our LCAO based band gap is higher than reported experimental value (3.93 eV) [12] deduced from optical spectroscopy method. The total and partial DOS (Fig. 2b) using LCAO-PWGGa approach show that the valence region between -6 eV to $E_F$ is mainly dominated by the Ta-5d and O-2p states and prove strong hybridization between 5d and 2p states of Ta and O atoms, respectively. Li-2s states are observed to have small contribution in both (VB and CB) regions. The CB region is merely formed due to contribution of 5d states of Ta atoms.
4. Conclusions
Compton profile and electronic structure (including density of states and energy bands) of LiTaO\textsubscript{3} are presented using 100 mCi \textsuperscript{241}Am Compton spectrometer and first-principles calculations, respectively. Theoretical profile based on LCAO-PWGGA approximation is found to be in close agreement with experimental profile showing pertinence of GGA approximation in explaining electronic response of LiTaO\textsubscript{3}. Further, direct band gap of 4.85 eV using LCAO-PWGGA approach is found to be 23.4\% higher than the experimental value.

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