Investigation of P-type transparent superconductivity in Layered $NaNbO_2$ compound.

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ABSTRACT

Development of p-type transparent conducting materials is a challenging issue in recent time. The known p-type transparent conductors unsatisfied both of high transparency and high conductivity nor exhibit superconductivity. Here, we have investigated the possibility of superconductivity along with the transparency of delafossite type layered $NaNbO_2$. We have reported the structural, electronics, lattice dynamics and optical properties of $NaNbO_2$. Calculated electronic band structure shows an indirect band gap of 1.5 eV. The phonon dispersion curves confirm the dynamical stability of $NaNbO_2$ as there is no imaginary frequency found throughout the Brillouin zone (BZ). Calculated dielectric constants and absorption coefficient shows absorption edge around 1.5 eV indicated its applicability in optoelectronic industries.

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INTRODUCTION

Search for new transparent conductors (TCs) is one of the most important subjects not only for practical use but also for advances in materials science [1]. In case of n-type TCs, a variety of materials have been developed and used in industry. For example, Sn-doped In_2O_3 (ITO) exhibits high conductivity (~6000 S cm^{-1}) and high transparency (~80%) [2]. In contrast to n-type TCs, however, p-type TCs are subjects of fundamental research since their performances are still low [3].

Zhang et al. [4] recently proposed new strategy for designing TCs based on transition-metal oxides (TMOs). In contrast to a traditional concept (taking ITO as an example, high-

mobility semiconductor In2O3 is doped with a small amount of Sn). On the basis of this strategy, perovskite-type have been found to be good TCs, both n- and p-type . However, the studies have been so far limited to the perovskite-type TMOs. Thus, further investigation on other TMOs will pave a way for better p-TC performances.

Then, an experimental study suggested a emergent superconductivity as well as a sign of transparency in $LiNbO_2$. $LiNbO_2$ is also layered structure and it belongs to the same space group as delafossite. Here we have systematically studied the superconductivity and electron phonon interaction of $NaNbO_2$. In this paper we have calculated the structural, electronics, lattice dynamics, electron phonon interaction and optical properties of delafossite type $NaNbO_2$.

COMPUTATIONAL METHODS

All calculations in the present work were performed using a plane wave pseudopotential method based on the density functional theory (DFT) [5] implemented in the Quantum Espresso code. [6] Generalized gradient approximation (GGA) was used for the exchange-correlation functional [7] in which the energy was parameterized by Perdue, Burke, and Ernzerhof (PBE) within norm-conserving pseudopotentials.

The energy cut-off for the wave function and charge density was 70 Ry. In reciprocal lattice space integral calculations, we used 10 x 10 x 10 k-point grids in the Monkhorst-Pack scheme [8]. Structural optimization was performed by a constant pressure variable cell using the Parrinello—Rahman method [9]. The unit cell was relaxed under the Broyden-Fletcher—Goldfarb—Shannon (BFGS) algorithm [10]. The calculations of vibrational properties are performed by employing the density functional perturbation theory (DFPT) [11]. Furthermore, the calculation of optical properties is carried out using the Karmers-Kronig transformation and the critical temperature calculations performed using the electron phonon

Wannier (EPW) code.

RESULTS AND DISCUSSION

A. Structural properties

$NaNbO_2$ possesses a hexagonal crystal symmetry with the Pc3/mmc space group. The crystal geometry of $NaNbO_2$ is presented in Fig. 1. The unit cell of layered $NaNbO_2$ contains 8 atoms with two Na, two Nb, four O.

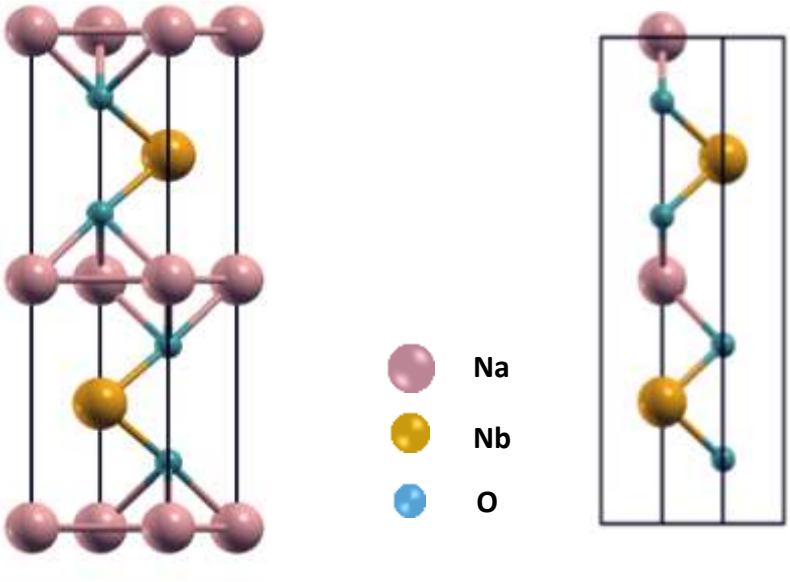

FIG .1 Crystal geometry of $NaNbO_2$

In the unit cell a Na atom bounded with two O atom, and a Nb atom also bounded with two O atoms. The bond lengths between Na-O is 2.32 Å and Nb-O is 2.20 Å. The observed angles of O-Nb-O is 79.030, O-Na-O is 99.020 and Na-O-Nb is 96.440. The structure of NaNbO2 which are shown in Fig. 1 is a layered structure similar to the previously synthesized $LiNbO_2$.

B. Electronic band structure

The electronic band structure is a key to understand the inherent electronic properties of a condensed matter system. The electronic band structure helps to estimate the magnetic moment of an electron and the effective mass of electrons and holes. We now the discuss the electronic structure of $NaNbO_2$. The calculated electronic band structure of NaNbO2 is shown Fig. 2. It clearly shows that the NaNbO2 is an indirect bandgap semiconductor with 1.55 eV band gap. The electronic band structure is calculated along the high symmetry direction of the Brillouin zone (BZ) and the considered path is along Γ-M-K-H-Γ directions.

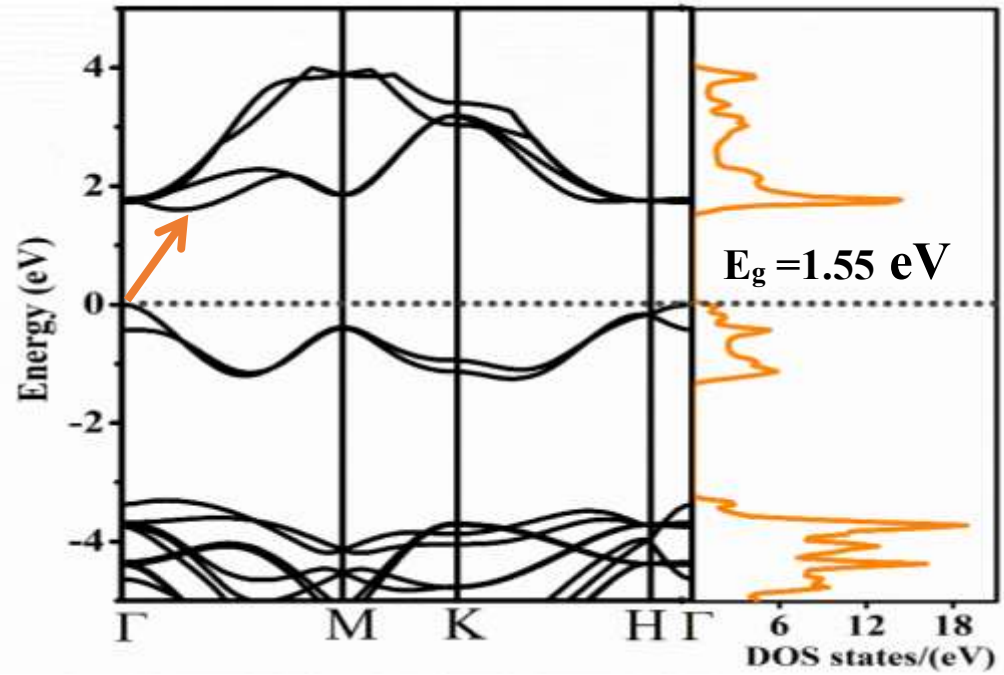

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Fig. 2. Electronic band structure and Density of States of $NaNbO_2$.

Here, we observed that the maxima of valence band is found at **Γ** point and the minimum of the conduction band is observed between the **Γ-M** direction which confirms the indirect nature of this compound. Unlike other delafossite compounds the $NaNbO_2$ shows dispersive bands near the Fermi level which indicates the low hole effective mass and further the high p-type conductivity. The calculated density of states (DOS) shown in right panel of the Fig. 2 also

confirm the band gap of 1.55 eV. The density of states illustrates the density of electronic states in full Brillouin zone (BZ).

C. Phonon Dispersion Curves and Superconducting Properties

Phonon dispersion curves (PDCs) are key components to investigate the lattice dynamics, atomic vibrations, electron-phonon interaction, thermal conductivity, phase transition and dynamical stability in various crystals and their low dimensional counterparts. [11]. In recent years PDCs are extensively used to study the dynamic stability of various composition and structure. To check the stability of NaNbO2 as well as the electron-phonon interaction constant (λ), we have calculated the phonon dispersion curves (PDCs) of NaNbO2 and presented them in Fig. 3. NaNbO2 has real frequencies in the entire Brillouin zone (BZ) indicating their dynamical stability. There are 8 atoms in unit cell resulting into 24 phonon branches including 3 acoustic and 21 optical branches

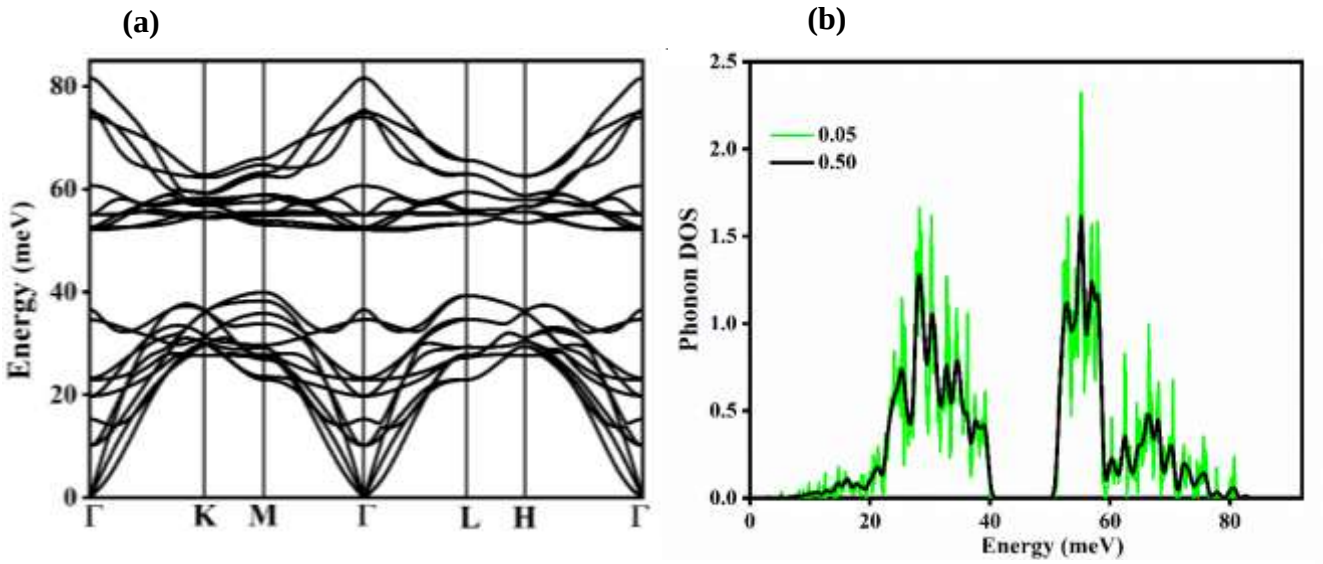


Fig. 3 (a) The phonon dispersion curve (b) Phonon density of states of $NaNbO_2$.

The PDCs of $NaNbO_2$ can be divided into two region that is the lower optical as well as the upper optical region. The lower optical region is ranging from 10 meV to 40 meV,

between 40 meV to 50 meV there is a gap in this PDCs. Between 50 meV to 80 meV the phonon referred as upper optical region. Further, we have calculated the phonon density of states (Phdos) and shown in Fig. 3(b). The Phdos shows the distribution of phonons in the entire BZ. The calculated Phdos reflects all the important features of PDCs of $NaNbO_2$.

The Na and Nb atoms possess the D_{3d} site symmetry, while the O atoms occupy the C_{3v} site symmetry. The factor group analysis yields the following irreducible representation of $NaNbO_2$ at the zone center.

$$\Gamma = \boldsymbol{A_{1g} + E_g + 3A_{2u} + 3E_u} \qquad \textbf{(1)}$$

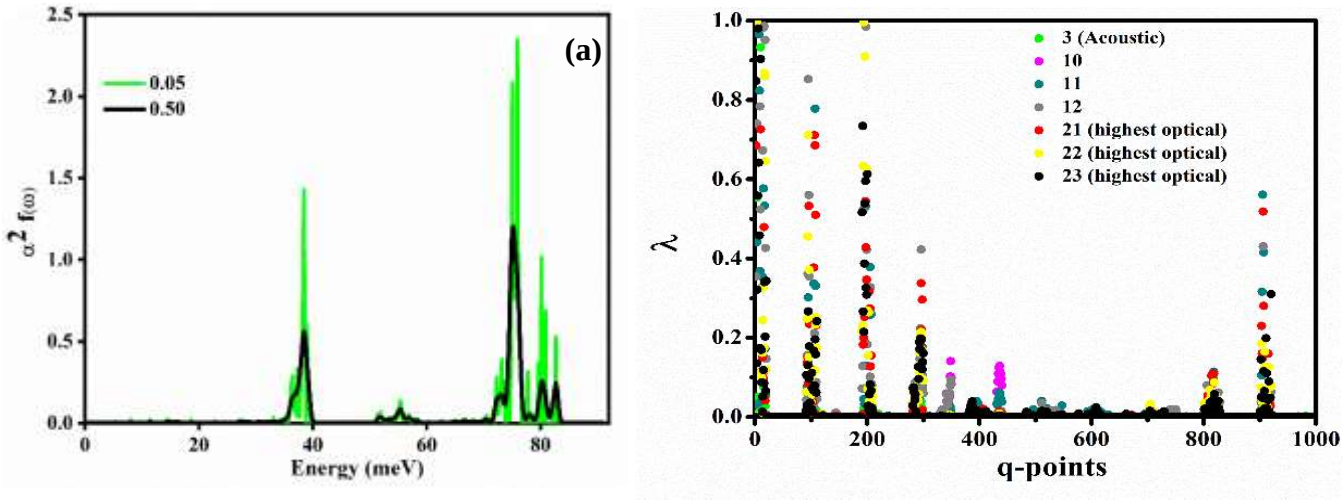


Fig. 4 (a) Eliashberg spectral function for $NaNbO_2$ at different phonon smearing (b) Mode resolved electron phonon coupling constant λ.

Calculated Eliashberg spectral function ($\alpha^2 f$) and electron phonon coupling constant (λ) for $NaNbO_2$ are shown in Fig. 4 (a-b) respectively. It can be seen from Fig. 4(a) that the highest peak locates around 70 meV, originated due to the strongly coupled highest optical modes. By integrating $\alpha^2 f$, we find the electron phonon coupling constant λ. Here, it can be seen from Fig. 4 (b) that the electron phonon coupling constant (λ) shows maximum values for the highest optical modes. The red, yellow and black dots in Fig. 4 (b) shows the electron

phonon coupling strength by successive highest optical modes. We have calculated the overall electron phonon coupling constant (λ) of 0.123 for a screened Coulomb interaction parameter of μ* = 0.1. The estimated Tc using McMillian-Allen-Dyne's formula (Eq. 2) is around 0.4 μK.

$$Tc = \frac{\omega log}{1.2}\exp\left[\frac{-1.04(1+\lambda)}{\lambda(1-0.62\mu*)-\mu*}\right] \quad (2)$$

D. Optical properties

Due to a suitable bandgap of 1.55 eV of NaNbO2 it is noteworthy to study their optical properties, which provide a picture about the interaction of light with the system, and its useful in optoelectronic devices**.**

1.Dielectric constants

It is well known that the optical properties of a system can be obtained by the complex dielectric function (CDF). The real parte, $[\in_1 (\boldsymbol{\omega})]$ of the dielectric function follows the Kramers-Kronig transformation within the random phase approximation (RPA). Other optical properties can be derived from the CDF. The CDF is used to measure the Linear response to an external electromagnetic field with a small wave vector k, the optical properties can be gained from the same [12-13]. Expressions for the absorption coefficient, refractive index, coefficient of extinction, optical reflectivity, and loss spectra are presented in what follows:

$$\in (\boldsymbol{\omega}) = \in_1 (\boldsymbol{\omega}) + \in_2 (\boldsymbol{\omega}) \quad (1)$$

The imaginary part [$\in_2(\boldsymbol{\omega})$] of the dielectric function can be determined using an electronic band structure through the momentum matrix element and the joint density of states (JDOS) between the unoccupied and occupied wave functions within the selection rules and is given by

$$\in_2(\boldsymbol{\omega}) = \frac{2e^2\pi}{\Omega\in_0} \sum \boldsymbol{k, c, v} \; |\boldsymbol{\psi}_k^c < \boldsymbol{u} \times \boldsymbol{r} > \boldsymbol{\psi}_k^v|2 \; \boldsymbol{\delta}(\boldsymbol{E}_k^c - \boldsymbol{E}_k^v - \boldsymbol{E}) \qquad (2)$$

The imaginary part of the dielectric function in the above equation depends oj the JDOS and momentum matrix element. The Kramers-Kronig relation is used to calculate $\in_1(\boldsymbol{\omega})$ from $\in_2(\boldsymbol{\omega})$ of the dielectric function [14]

$$\in_1(\boldsymbol{\omega}) = 1 + \frac{2}{\pi} \boldsymbol{P} \frac{\int \omega' \in_2(\omega')}{\omega'^2 - \omega^2} \boldsymbol{d\omega'} \qquad (3)$$

The absorption coefficient α(ω) is obtained directly from the dielectric function $\in(\boldsymbol{\omega})$,

$$\boldsymbol{\alpha(\omega)} = \frac{\sqrt{2\omega}}{c} \left[\sqrt{\in_1^2 + \in_2^2 + \in_1} \right] = \boldsymbol{\alpha} = \frac{2\omega k}{c} = \frac{4\omega k}{\lambda 0} \qquad (4)$$

Where c is the speed of light ,as mentioned above ,all other optical parameter can be calculated by eqs. (2) and (3),

$$\boldsymbol{k(\omega)} = \frac{1}{\sqrt{2}} \; [(\in_1^2 + \in_2^2)^{\frac{1}{2}} - \in_1]^{1/2} , \qquad (5)$$

$$\boldsymbol{n(\omega)} = \frac{1}{\sqrt{2}} \; [(\in_1^2 + \in_2^2)^{\frac{1}{2}} - \in_1]^{1/2}. \qquad (6)$$

In the eq (5) and (6) , $\boldsymbol{k(\omega)}$ and $\boldsymbol{n(\omega)}$ represent the extinction coefficient and refractive index ,respectively . equation (7) is used to determine the reflectivity [R(ω)] and is given by

$$\boldsymbol{R(\omega)} = \frac{[(n-1)^2 + K^2]}{[(n+1)^2 + K^2]}. \qquad (7)$$

To estimate the energy loss by an electron ,we have calculated the loss function L(ω),which is given by

$$\boldsymbol{L(\omega)} = \frac{\epsilon_2(\omega)}{\epsilon_1^2(\omega)+\epsilon_2^2(\omega)}. \qquad (8)$$

All optical properties can be calculated by the real and imaginary part of the dielectric function.

2. Real part $\epsilon_1\ (\omega)$ and imaginary part $\epsilon_2\ (\omega)$ of the dielectric function

The real and imaginary dielectric function of $NaNbO_2$ compound is presented in the Fig. 5. It clearly seen that for both real and imaginary dielectric function reaches maxima at a lower energy range and then reaches minima at higher energy range. Hear the maximum peaks are due to the electronic transitions from the top of valence band to the bottom of the conduction band.

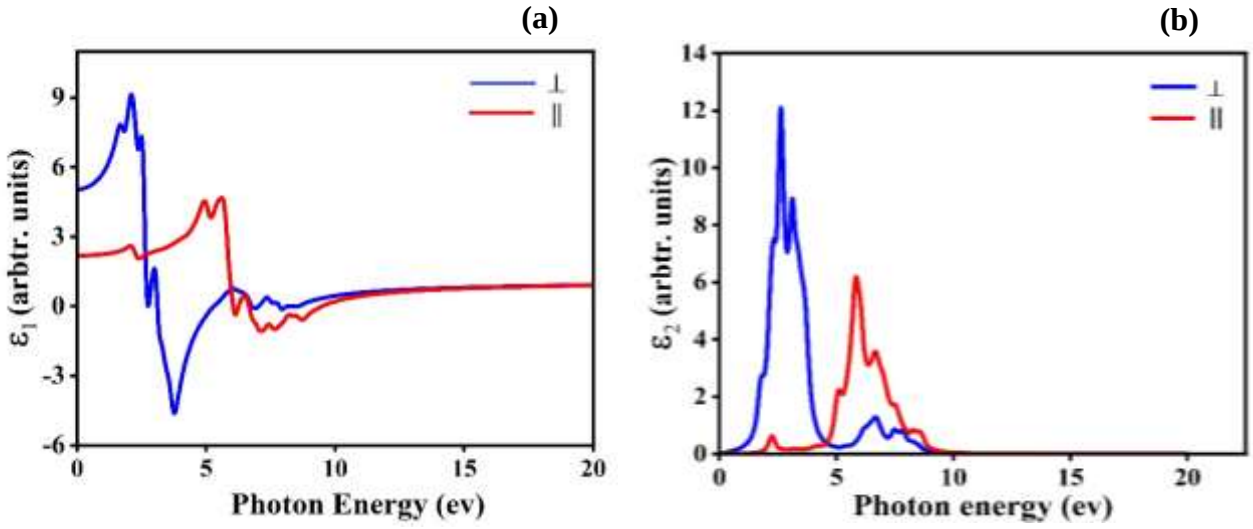


FIG. 5(a) Real part of dielectric function ,5(b) imaginary part of dielectric function

3. Absorption coefficient α (ω)

To have further insight into the possibilities of delafossite compounds for photovoltaic conversion applications, we have studied the absorption spectrum in the visible region and other corresponding to photon energy up to 14 eV, which is presented in Fig. 6.

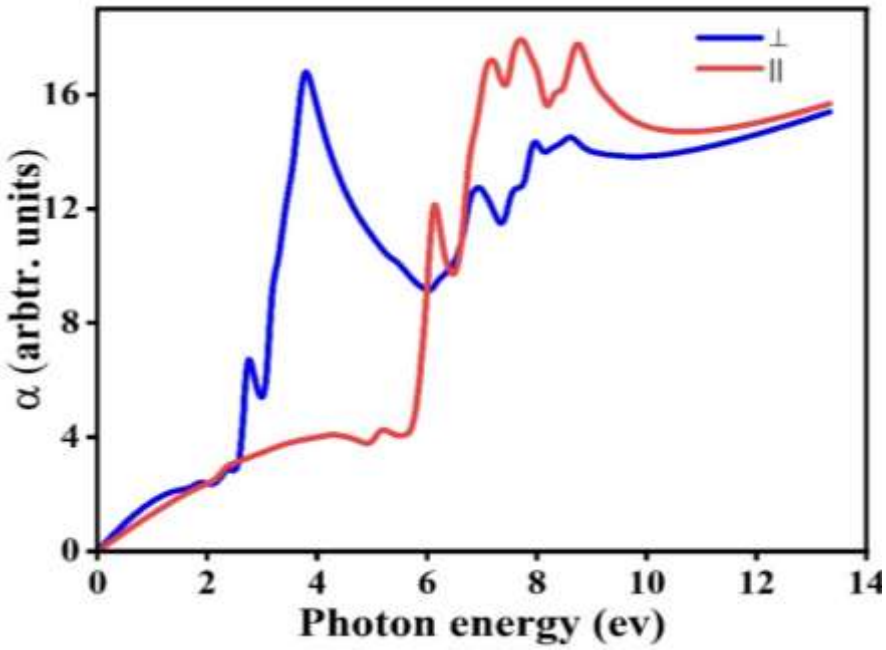


FIG. 6. Absorption coefficient of $NaNbO_2$

The absorption coefficient defines the absorptive nature of the materials toward light. Fig.6 indicate that $NaNbO_2$ compound is anisotropic in nature. The threshold value for the perpendicular component is near to 2.0 eV and the threshold value for parallel component is near to 2.4 eV. The threshold value indicates the visible light absorption. Which further, suggests its applications in photovoltaics.

4. Refractive index n(ω) and extinction coefficient k(ω)

The refractive index is calculated to analyze the polarization of the compound which is shown in Fig .7(a).

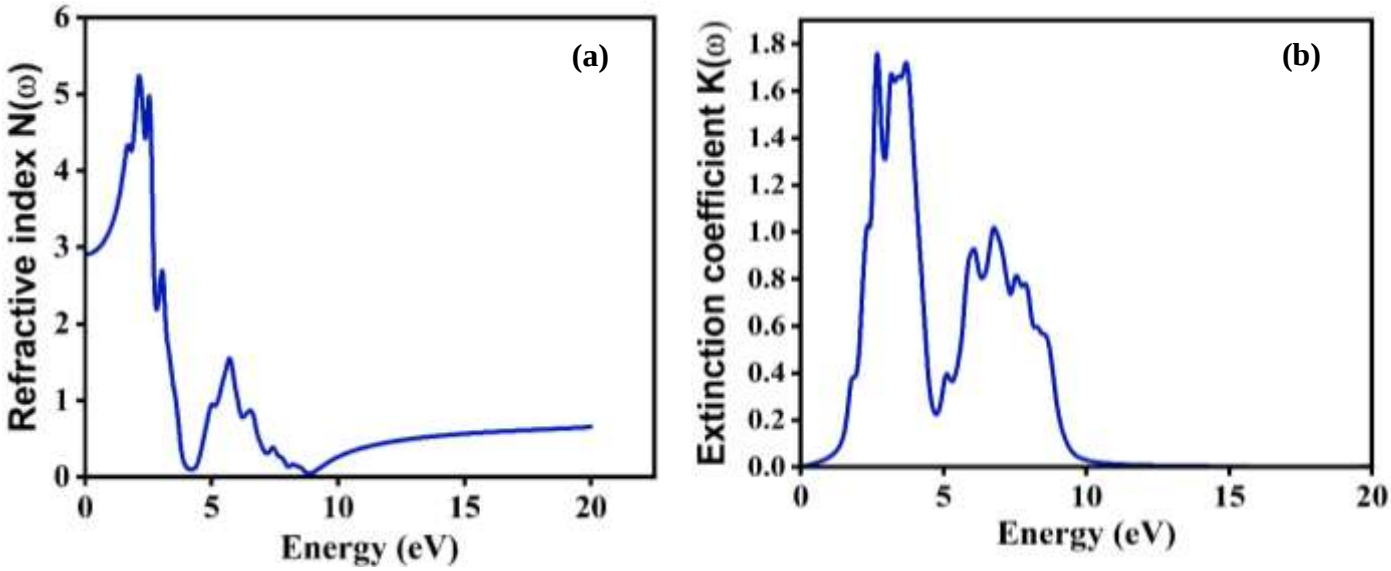


FIG. 7. (a) refractive index of $NaNbO_2$. (b)Extinction coefficient of $NaNbO_2$

The extinction coefficient k(ω)calculated up to 20 eV photon energy for $NaNbO_2$ compound is shown in Fig. 7(b). the magnitude of extinction coefficient increase with increasing incident photon energy. The extinction coefficient decreases in the ultraviolet region (high energy region), indicating the decay of oscillation amplitude of electric field. The extinction coefficient shows how the oscillation amplitude of electric field decay in relation with incident photon energy.

5. Optical reflectivity R(ω) and Loss spectrum L(ω)

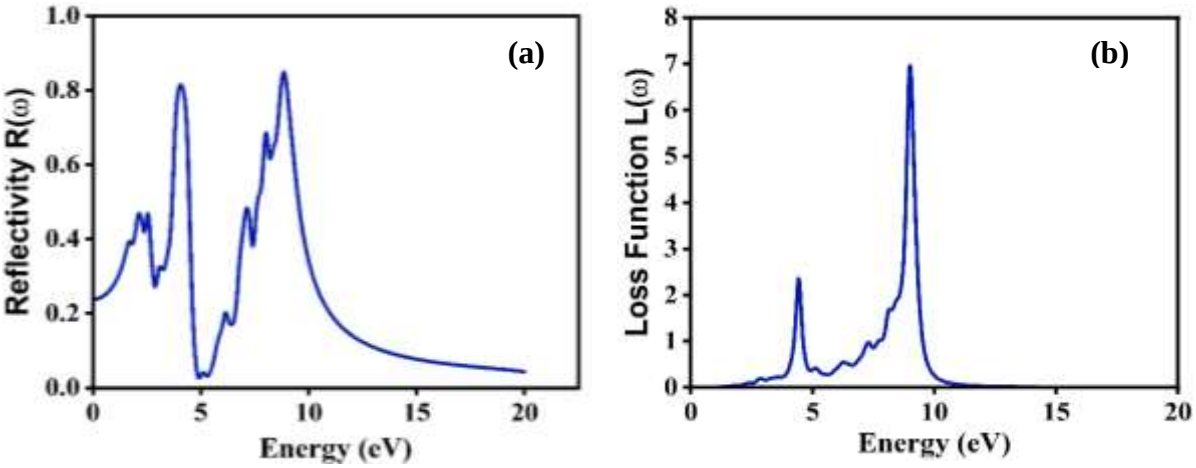
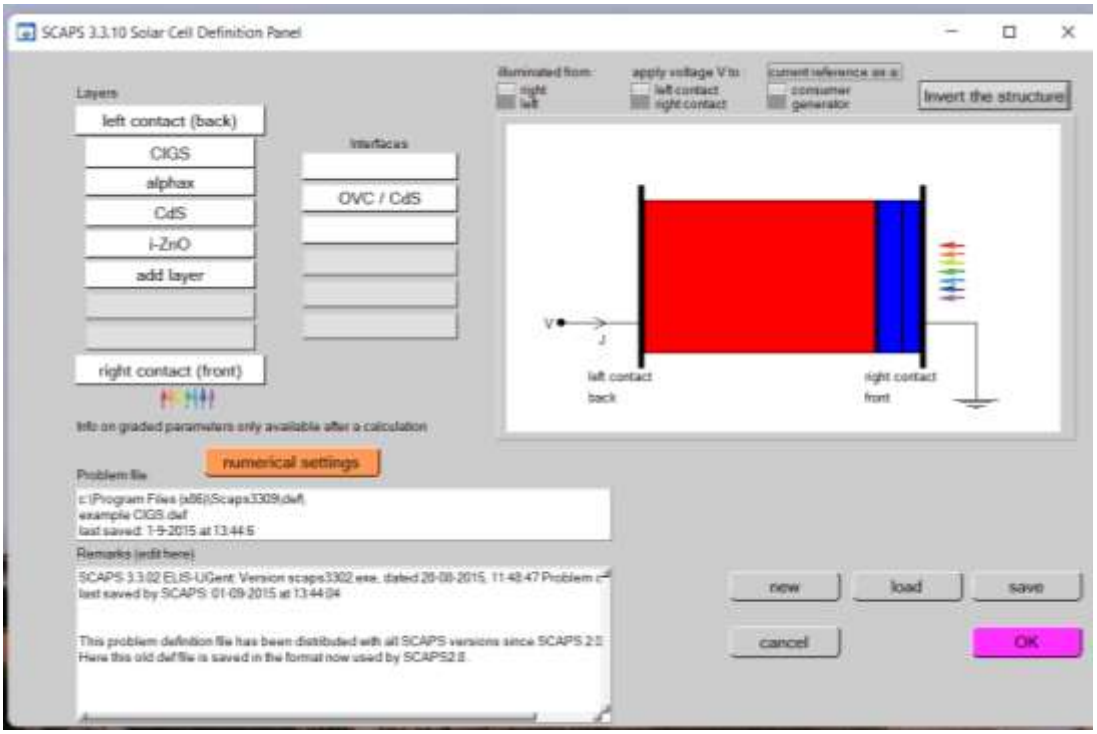


FIG. 7. (a) Reflectivity spectrum of $NaNbO_2$ (b) Loss spectrum of $NaNbO_2$.

The optical reflectivity of $NaNbO_2$ along with parallel and perpendicular component of polarization is shown in Fig.8(a) and Fig.8(b) shows the energy loss spectra corresponding to the photon energy up to 20 eV. The energy loss spectra define the loss of energy by an electron when passing through a homogenous dielectric material.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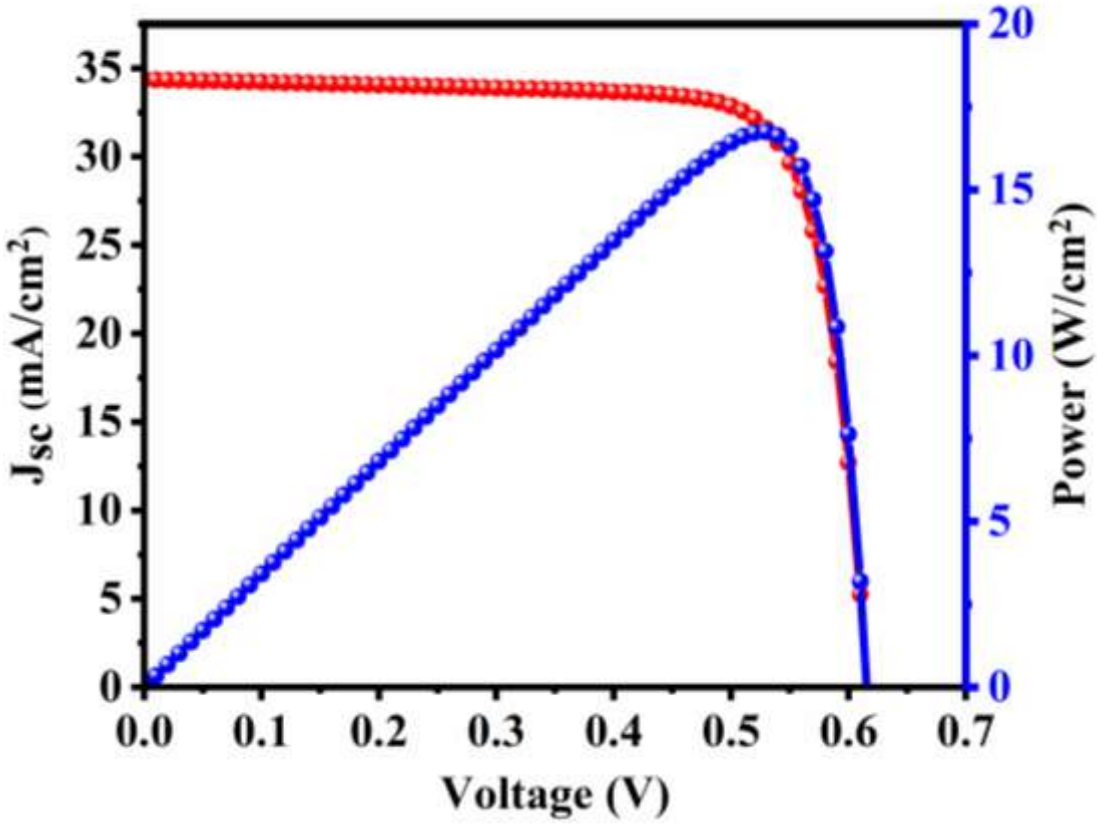
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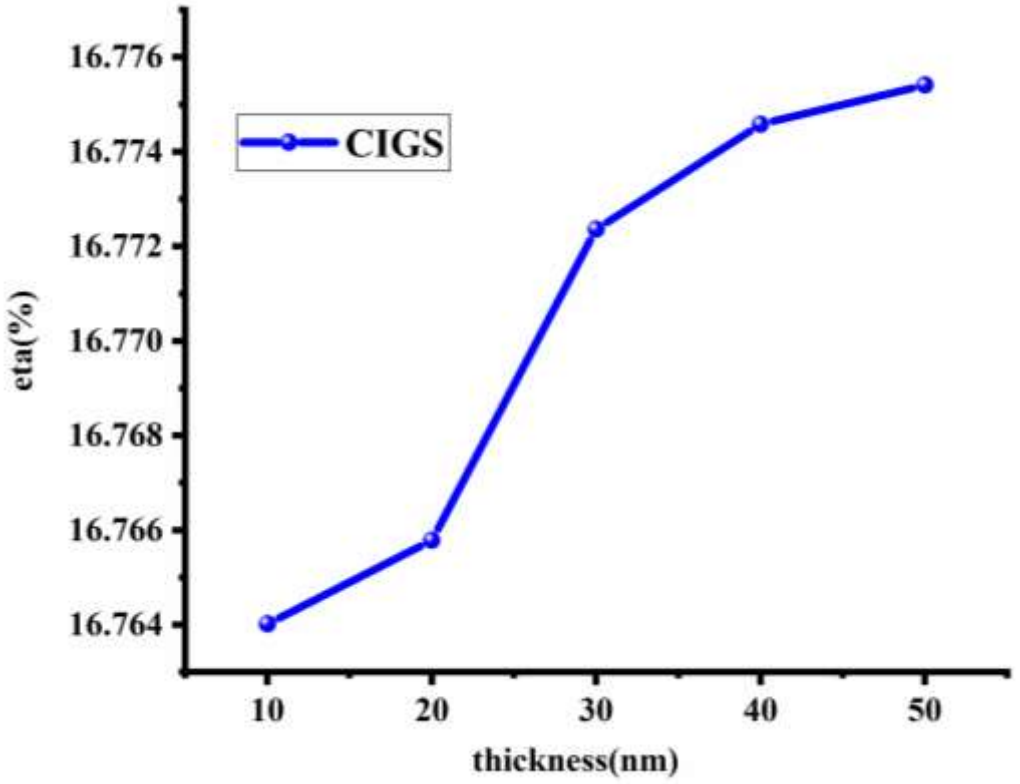
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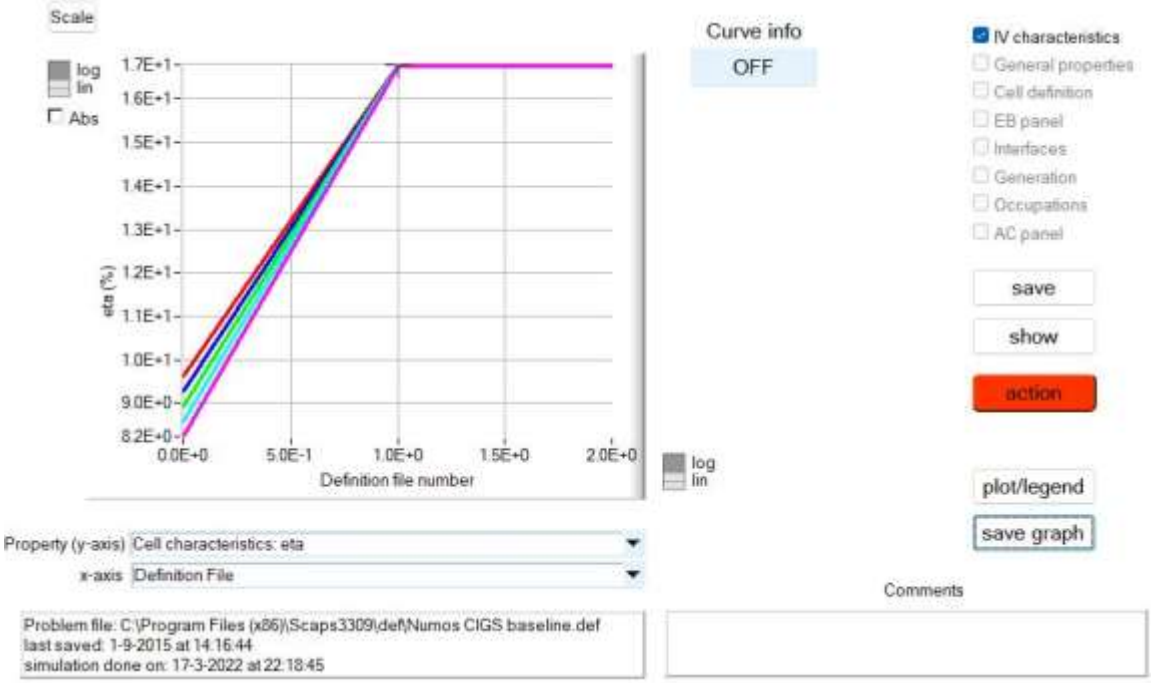
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Conclusions

In summary we have investigated the structural, electronics, lattice dynamics electron phonon coupling and optical properties of layered $NaNbO_2$ compound. The calculate electronic band gap of this compound is 1.5 eV which is indirect in nature. The unique structural geometry and bonding of Niobium (Nb) and oxygen (O) provide significant p-d hybridization which can be confirmed by partial density of states. Highly dispersive valence band indicates the low hole effective mass which further indicates the high p-type conductivity. The phonon dispersion curves and phonon density of states reveal that the $NaNbO_2$ is dynamically stable. Further, electron phonon coupling constant and transition temperature (T_c) is calculated. The electron-phonon coupling constant λ is found 0.123 and corresponding T_c is found to be 0.4 μK. The results of dielectric constant and absorption coefficient of $NaNbO_2$ indicates the visible light absorption which is useful for solar energy convertors as well as photocatalysis.

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