



## Diffuse reflectance spectroscopy: An effective tool to probe the defect states in wide band gap semiconducting materials



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### ABSTRACT

Optical properties of widely used semiconducting oxides namely; TiO<sub>2</sub>, ZnO and ZrO<sub>2</sub> were investigated using diffuse reflectance spectroscopy (DRS). Prior to the optical absorption measurements, the structural purity of these samples was examined using powder x-ray diffraction experiments carried out on Indus-2 synchrotron source. It is observed that all the studied samples are structurally pure. The DRS of all the studied samples show an extra peak much below fundamental band gap. In order to understand the origin of the said low energy peak, the theoretical optical absorption spectra for these samples have been simulated. The simulations were performed using density functional theory, considering, ideal as well as defected systems i.e. by considering vacancy at all possible sites (for TiO<sub>2</sub> we have considered the vacancy at Ti site and also at O site taking in to account surface and bulk effects). It is observed that the simulated optical spectra show very similar feature as that of experimental optical absorption for oxygen vacancy. Photoluminescence spectroscopy further supports the presence of defect states in the studied samples. Thus; it appears that the diffuse reflectance spectroscopy is a useful tool to probe the signature of defects present in the sample.

### 1. Introduction

The transition metal oxides have been extensively studied, because of their technical importance and the fundamental interest [1,2]. There has been increasing interest in the optical properties [3–5] of functional semiconducting oxide materials for their potential use as a transparent conductive oxide material, solar cell/photovoltaic material etc [2]. The band gap ( $E_g$ ) of any semiconductor material is an important feature of that material to assess its applicability for the devices. Further for various critical applications, it is important to characterize these materials especially for defect etc., as many of the properties of these materials are controlled by the defects. It is also well known and observed experimental fact that the behavior of the defects is different in different materials, for example, in case of MgO oxygen defects leads to excess electrons which are localized on its surface; but are de-localized in case of TiO<sub>2</sub> [6]. In the case of oxide semiconductor materials the signature of these defect have been reported through valence band spectroscopy [7], Raman spectroscopy [8], photoluminescence spectroscopy [9] etc. Interestingly, these defects leads to an extra states

(acceptor or donor level) between valence and conduction band [10]. Even though the signature of the defect is visible in above mentioned experimental data but with these techniques it is difficult to predict the site-specific defect i.e. whether the signature is due to Ti defect or oxygen defect in case of TiO<sub>2</sub>. This requires a high-resolution imaging in transmission electron microscopy, atomic force microscopy or scanning tunneling microscopy etc.

Recently, optical spectroscopy has been extensively used to probe the electronic excitations in solid samples i.e. to probe the band gap [4,5,11]. In case, if any acceptor or donor level is present in the sample due to the point defects/vacancies etc. it may get reflected in the optical absorption spectroscopy. Further, it is well known that the polycrystalline oxide samples have large surface area as compared to that of their single crystal counterparts and hence have more surface defect density. Thus, the possibility of detecting such defect states in polycrystalline samples appears to be higher as compared to their single crystal counterparts.

Keeping above in mind, in the present study, we have systematically investigated three different and widely used polycrystalline transition

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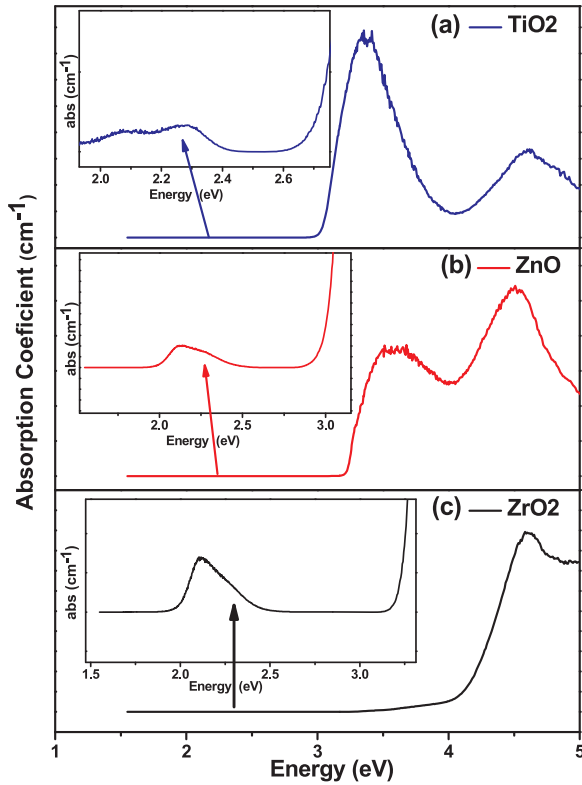


Fig. 1. Diffuse reflectance spectra for (a) TiO<sub>2</sub> (b) ZnO (c) ZrO<sub>2</sub>. Inset of each figure shows the magnified view of low energy region of optical absorption spectra, clearly showing the presence of absorption state in low energy region of spectra.

metal oxides using namely; ZnO, TiO<sub>2</sub> and ZrO<sub>2</sub> using diffuse reflectance spectroscopy. The optical absorption spectra for all the studied powder samples show a peak much below fundamental band gap edge. In order to understand the origin of the above discussed low energy peak, the optical absorption spectra of these samples were simulated using first principle density functional theoretical calculations (DFT) under generalized gradient approximation (GGA) considering  $3 \times 3 \times 2$  super cell. All the simulations were performed considering ideal as well as defected structure i.e. by considering vacancy at all possible sites, for example for TiO<sub>2</sub> we have considered the vacancy at Ti site and at O site. It is observed that the simulated optical spectra show very similar feature as that of experimental optical absorption for oxygen vacancy. Thus, it appears that the optical absorption spectroscopy is very useful and sensitive tool to probe the signature of defects present in the sample. It is also observed that oxygen defects are inherently present in poly crystalline oxide samples.

## 2. Experimental details

### 2.1. Sample preparation and characterization

High purity samples (99.95% pure) of ZnO, TiO<sub>2</sub>, and ZrO<sub>2</sub> were procured from Sigma Aldrich. The structural phase purity of these samples was confirmed through powder x-ray diffraction studies carried out using angle dispersive x-ray diffraction beamline BL12 at Indus-2 synchrotron x-ray source [12–14].

### 2.2. UV–VIS spectroscopy

The optical absorption spectra of prepared samples have been measured using diffuse reflectance spectroscopy (DRS) [4,5] measurements. DRS experiments have been performed in the wavelength range

of 190–1100 nm by means of a Cary-60 UV–VIS–NIR spectrophotometer equipped with Harrick Video-Barrelino diffuse reflectance probe.

### 2.3. Methods and computational details

The first-principles calculations are performed by employing FP-LAPW [15] approach implemented in WIEN2K code [16]. For present DFT [16,17] calculations, generalized gradient approximation (GGA) [18,19] was selected as an exchange-correlation potential. In the present calculations, we used  $R_{\text{MT}}K_{\text{max}} = 7$ , which determines matrix size (convergence), where  $K_{\text{max}}$  is the plane wave cut-off and  $R_{\text{MT}}$  is the smallest of all atomic sphere radii. The muffin-tin radii (MT) for Zn, Ti, Zr were chosen as 1.85, 1.85, 2.08 and 1.64, 1.67, 1.85 for O in ZnO, TiO<sub>2</sub>, ZrO<sub>2</sub> respectively. The self-consistent calculations were considered to be converged when the total energy of given structure is stable within  $10^{-3}$  mRy. The k-mesh size of  $3 \times 3 \times 3$  has been used in the irreducible Brillion zone (IBZ). For Zinc oxide we have used HSE + U [20] exchange-correlation to compute the electronic density states as GGA + U [18,19] and simple HSE could not predict the correct value of experimental band gap. optical properties (absorption coefficient) of oxide structures modeled with and without vacancies has been calculated through complex dielectric functions using the formalism of Ehrenreich and Cohen [21]. In order to calculate the dielectric properties we have used the self-consistent field for each structure calculated using GGA + U/ HSE + U [20]. The dielectric function is given as

$$\varepsilon(\omega) = \varepsilon_1(\omega) + \varepsilon_2(\omega), \quad (1)$$

Expression for calculating optical absorption coefficient  $\alpha(\omega)$  from dielectric constant [22,23] is as follows -

$$\alpha(\omega) = \sqrt{2}\omega(\sqrt{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} - \varepsilon_1(\omega))^{1/2}, \quad (2)$$

## 3. Results

Fig. 1 shows the experimental diffuse reflectance spectra (DRS) for (a) TiO<sub>2</sub> (b) ZnO and (c) ZrO<sub>2</sub>. The obtained DRS has been converted into its corresponding absorption spectra by using the following Kubelka–Munk and Tauc relations [24–26],

$$F(R_{\infty}) = \frac{(1 - R_{\infty})^2}{2R_{\infty}}, \quad (3)$$

where;  $F(R_{\infty})$  is the Kubelka–Munk function ( $R_{\infty} = R_{\text{sample}}/R_s \tan \alpha$ ). The Kubelka–Munk function, which is proportional to the absorption coefficient ( $\alpha$ ), can be written as-

$$F(R_{\infty}) \propto \alpha \propto \frac{(h\nu - E_g)^{1/n}}{h\nu}, \quad (4)$$

$$(\alpha h\nu)^n = A(h\nu - E_g). \quad (5)$$

Inset of each figure shows a magnified view of absorption spectra over a selected low energy range. A weak but clear absorption feature is visible for all three studied samples, as clear from the inset of Fig. 1. At this juncture it is very important to note that recently Y. Li et al. [27] have shown the effect of point defects on the optical properties of LiNbO<sub>3</sub> using first principle studies and observed that point defects at Li, Nb and O sites leads to the peak in the theoretical optical absorption spectra. The position and the intensity of these peaks are found to be dictated by the type of point defect i.e. defect due to Li, Nb and O etc. Keeping this in view we have performed the first-principles calculations as discussed above.

Figs. 2–4 represents the comparison of experimentally observed and theoretically generated optical spectra for the ideal and for the sample having defects at transition metal site and oxygen site. From these figures it is clear that the pure sample without any defects do not show any peak in the absorption spectra below band gap edge. Whereas; the samples with defect at transition metal element site and oxygen site

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