# Spectrophotometric method for optical band gap and electronic transitions determination of semiconductor materials

Nicola Sangiorgi [a, b, *], Lucrezia Aversa [c], Roberta Tatti [c], Roberto Verucchi [c], Alessandra Sanson [a]

[a] CNR-ISTEC, Institute of Science and Technology for Ceramics, National Research Council of Italy, Via Granarolo 64, 48018 Faenza, Italy
[b] Department of Chemical Science and Technology, University of Rome "Tor Vergata", Via della Ricerca Scientifica 1, 00133 Rome, Italy
[c] CNR-IMEM, Institute of Materials for Electronics and Magnetism, Via della Cascata 56/C, 38123 Trento, Italy

## ARTICLE INFO

## ABSTRACT

The optical band gap energy and the electronic processes involved are important parameters of a semiconductor material and it is therefore important to determine their correct values. Among the possible methods, the spectrophotometric is one of the most common. Several methods can be applied to determine the optical band gap energy and still now a defined consensus on the most suitable one has not been established. A highly diffused and accurate optical method is based on Tauc relationship, however to apply this equation is necessary to know the nature of the electronic transitions involved commonly related to the coefficient $n$. For this purpose, a spectrophotometric technique was used and we developed a graphical method for electronic transitions and band gap energy determination for samples in powder form. In particular, the $n$ coefficient of Tauc equation was determined thorough mathematical elaboration of experimental results on $TiO_2$ (anatase), ZnO, and $SnO_2$. The results were used to calculate the band gap energy values and then compared with the information obtained by Ultraviolet Photoelectron Spectroscopy (UPS). This approach provides a quick and accurate method for band gap determination through $n$ coefficient calculation. Moreover, this simple but reliable method can be used to evaluate the nature of electronic transition that occurs in a semiconductor material in powder form.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

In the past few years a lot of new materials for energy conversion from renewable resource have been developed [1–7], with an increasing interest in those showing nanoscale microstructure with unique electrical, magnetic and optical properties. Most of these materials are semiconductors, with valence band and conduction band separated by the so-called band gap energy ($E_g$) [8]. $E_g$ is therefore a key property for a material to be used into technologies based on the conversion of sunlight into energy. When the sunlight is absorbed, several type of electronic transitions can occur, depending on the band alignment of the material. In a crystalline materials, unlike atoms or molecules, we need to take account of an infinite array of atomic potentials arranged on an infinite periodic lattice to properly locate and define the energy levels. The periodicity of the lattice is reflected into the probability distribution of the electrons that must also be periodic. The lattice is infinite and the electrons typically form delocalised states that extend through the crystal. One type of wavefunction that describe these conditions is Bloch wavefunction through wavevector (k) and the energy map (E) against wavevector k is the crystal band structure [8]. When the conduction band and valence band occur at the same value of k, and the photon have a sufficient energy to create an electron-hole pair, the electron is promoted to the conduction band by a direct transition and the semiconductor is called a direct bad gap material. On the other hand, if the minimum of conduction band and maximum of valence band occur at different values of k, the promotion of an electron from the valence to conduction band would cause a change in its momentum, and this must be supplied by a phonon (i.e. a lattice vibration). This type of absorption is related to indirect transition and the semiconductor is called an indirect band gap material [9].

* Corresponding author. CNR-ISTEC, Institute of Science and Technology for Ceramics, National Research Council of Italy, Via Granarolo 64, 48018 Faenza, Italy.
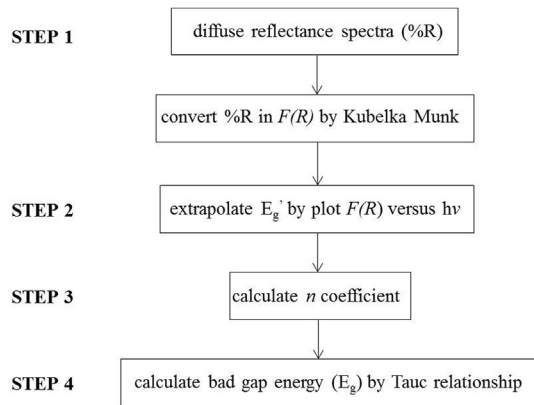E-mail address: nicola.sangiorgi@istec.cnr.it (N. Sangiorgi).

STEP 1

diffuse reflectance spectra (%R)

convert %R in $F(R)$ by Kubelka Munk

STEP 2

extrapolate $E_g'$ by plot $F(R)$ versus $h\nu$

STEP 3

calculate $n$ coefficient

STEP 4

calculate bad gap energy ($E_g$) by Tauc relationship

**Fig. 1.** Flow sheet of method developed.

The indirect band gap reduces the optical absorption, compared to direct gap semiconductors, because "extra energy" is required for an electron promotion. The knowledge of these electronic transitions is especially important for new synthesized materials applied in photovoltaic devices, water-splitting and perovskite solar cells [10–12], and it is the most important variable for an accurate optical band gap determination. Several different spectrophotometric methods have been used in literature to graphically determine the band gap energy but not unanimous consensus has been reached regarding the best approach [13,14]. A comparative study of different spectrophotometric analysis for TiO₂ was made by López

[13] and the results pointed out the importance of the choice of an appropriate graphical method to obtain reliable results. One of the most accurate approach considers the diffuse reflectance spectroscopy (Kubelka Munk theory) and the mathematical elaboration through Tauc equation in the form [13,15–21]:

$$\alpha h\nu = A \left(h\nu - E_g\right)^n \tag{1}$$

where $\alpha$ is absorption coefficient, h is the Planck's constant (J·s), A is the absorption constant, $\nu$ is the light frequency (s$^{-1}$), and $E_g$ is band gap energy (eV). The $n$ exponent in Eq. (1) is connected to the type of possible electronic transitions and its value is 2 for an indirect allowed transition, 3 for an indirect forbidden, 1/2 for a direct allowed and 3/2 for a direct forbidden transition.

In order to use the Tauc relationship to determine the band gap energy it's therefore important to know the correct value of $n$ in Eq. (1). Two main spectrophotometric procedures can be used to calculate its value, the first is through absorbance measurements whereas the second considers a mathematical elaboration of the Tauc relationship. In the first method is necessary to acquire the absorbance spectrum of the material of interest in form of pellets [22] or suspensions [17], but requires more sample preparation (e.g. stabilize the suspension) time while the second method provides the calculation of $n$ coefficient from original reflectance data [23], leading to higher precision.

In this work we present a mathematical and graphical extrapolation of $n$ coefficient from Tauc relationship. We elaborated a rapid and precise method for band gap determination for powder
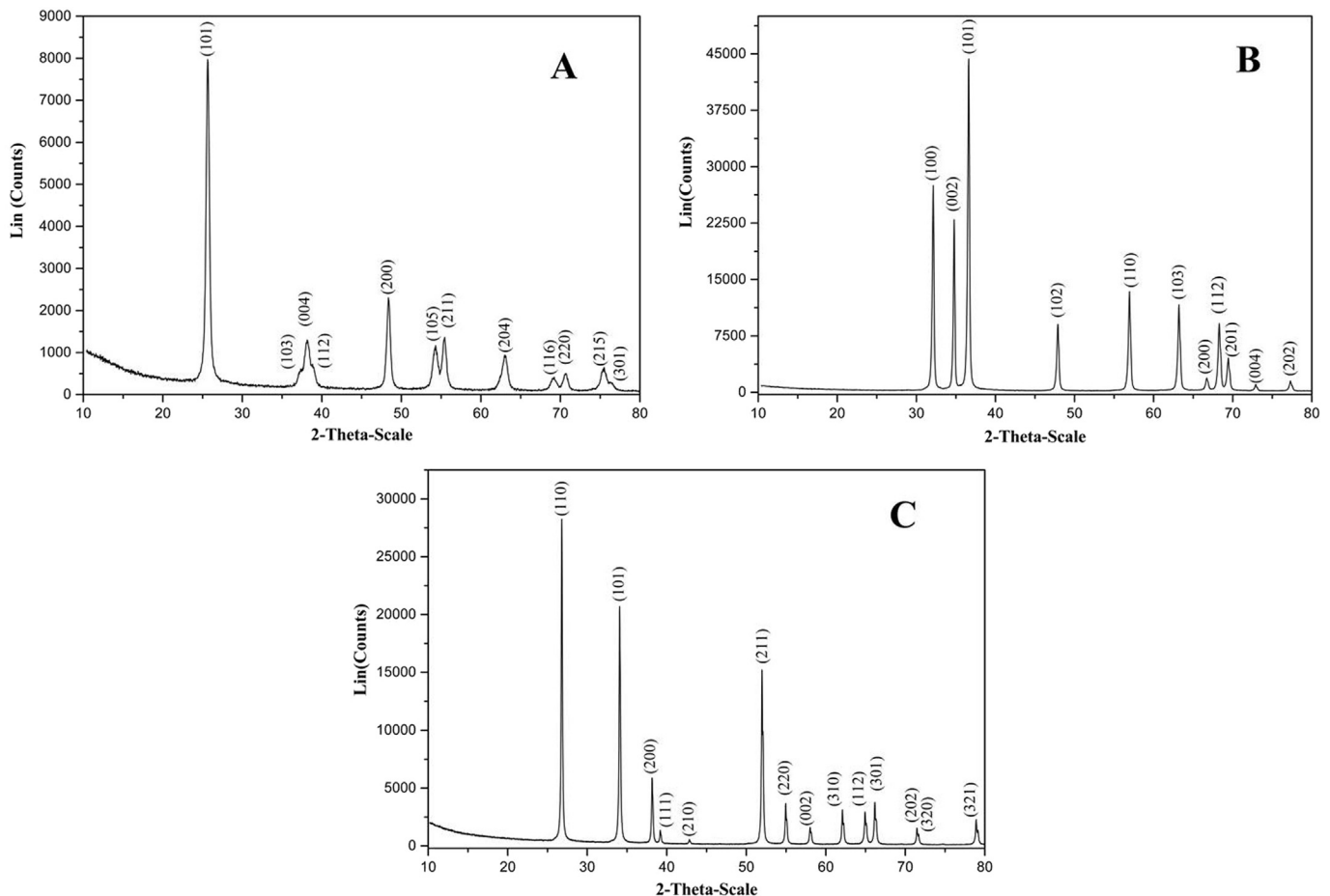


**Fig. 2.** Powders X-ray diffraction patterns of (A) TiO₂, (B) ZnO, (C) SnO₂.