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Assessing the amount of the anatase and rutile phases of TiO_2 by optical reflectance measurements

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ABSTRACT

The anatase (A) and rutile (R) phases of a series of titanium dioxide (TiO_2) samples were investigated by optical diffuse reflectance spectroscopy. The samples consisted of commercial A and R high-purity TiO_2 powders mixed together according to the $R_{mass}/(R_{mass} + A_{mass})$ rutile mass ratio. The optical reflectance spectra of the A + R TiO_2 mixtures are very distinctive and their derivatives presented a clear relationship with the rutile mass fraction – according to which the phase composition of TiO_2 can be estimated with good precision. The optical bandgaps of the A + R TiO_2 mixtures were also determined and correlated with the rutile mass ratio. In its current form, this work shows the potential of optical reflectance spectroscopy to (fast and reliably) estimate the amount of rutile (or anatase) phase in TiO_2-based materials.

Titanium dioxide TiO_2 is a very important semiconductor that exists, predominantly, in the anatase (A) and rutile (R) crystalline phases [1]. Accordingly, TiO_2 has been the basis of many successful applications in the fields of optical coatings [2], photovoltaics [3,4], photocatalysis [5,6], etc. Given their rather different properties, the relative amount of the A and R phases has a significant impact on the performance of real devices. In solar cell applications, for instance, owing to its higher electron mobility, superior surface area, and lower dielectric constant, the A phase is preferred over the R one. Furthermore, TiO_2 is a low-cost, temperature-resistant, chemically-inert semiconductor that (still) attracts great academic-technological interest. As a result, this work was intended to assess the amount of the rutile (or anatase) phase present in A + R mixed TiO_2 by optical reflectance spectroscopy. The optical bandgaps of the A + R TiO_2 samples were determined as well.

The samples considered in this work consisted of TiO_2 powder under the A and R high-purity (99.99%) phases. The starting A and R powders were weighted, mixed, and homogenized to obtain samples with different compositions, as defined by the $R_{Ratio}^{(mass)} = (R_{mass})/(R_{mass} + A_{mass})$ rutile mass ratio. Following this procedure, a total of 14 samples were achieved ranging from pure anatase (R0) to pure rutile (R100). The atomic structure of the current samples was investigated by x-ray diffraction and Raman scattering measurements, that confirmed the effective mixing of the A + R phases [7]. The optical reflectance measurements were carried out in a system comprised by a portable optical spectrophotometer (*Ocean Optics* HR4000), optical fibers-lenses, and integrating sphere. The measurements were taken at room-temperature and sample probed areas and spectral resolution stayed around 3 mm^2 (2 mm spot diameter) and below 10 nm, respectively. All spectra were

properly corrected by the optical response of the system (light source + diffraction grating + detector) to ensure 100% light reflection from a diffuse reflectance standard (Spectralon®).

The optical reflectance (henceforth $\Re$) spectra of some A + R TiO_2 samples are shown in Fig. 1(a). As can be seen, the spectra are very unique and contain details of the individual TiO_2 phases – as expected due to their A and R relative amounts. In view of the typical shape and behavior of the spectra, a promising way to assess the A and R phases of TiO_2 involves the derivative of $\Re$ in terms of the photon energy E (d$\Re$/dE). According to this approach, it became evident the presence of two main signals at 3.05 ± 0.05 eV (R-related) and at 3.30 ± 0.10 eV (A-related), and the scaling of these signals with the rutile mass ratio. Part of these features are displayed in Fig. 1(b)–(g) (for samples R0, R20, R43, R60, R80, and R100) that, additionally, shows the fitting of the R- and A-related contributions with Gaussian functions. The main results provided by the analysis of d$\Re$/dE, of all A + R TiO_2 samples, are presented in Fig. 2 – along with their optical bandgap values.

Traditionally, the optical (absorbance, transmittance, or reflectance) spectra of semiconductor materials can be used to determine the energy separation between the top of the valence band and the bottom of the conduction band or, the so-called optical bandgap E_{gap}. In the specific case of TiO_2, there is some debate relating the nature of the optical transitions (if direct or indirect) as well as regarding the proper method to determine E_{gap}.

Just to illustrate the point: whereas there is some agreement that bulk R-TiO_2 presents indirect optical transitions and $E_{gap} \sim 3.0$ eV [8], and that bulk A-TiO_2 exhibits direct transitions with $E_{gap} \sim 3.2$ eV [9]; these values are known to be highly influenced by the optical spectra

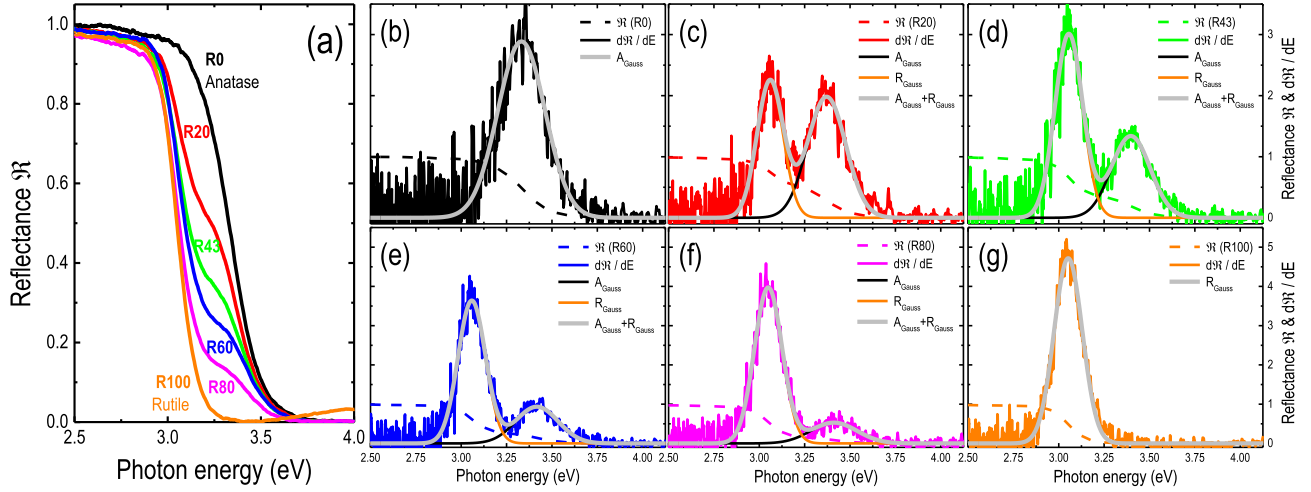**Fig. 1.** (a) Optical diffuse reflectance spectra $\Re$ of some A + R TiO$_2$ samples, and corresponding d$\Re$/dE curves and fittings with A$_{Gauss}$ and R$_{Gauss}$ Gaussian functions: (b) pure anatase (R0), (c) to (f) with increasing amounts of rutile (R20, R43, R60, and R80), and (g) pure rutile (R100). In (a) the spectra were corrected by the response of the system (*i.e.*, diffuse standard and optical setup).
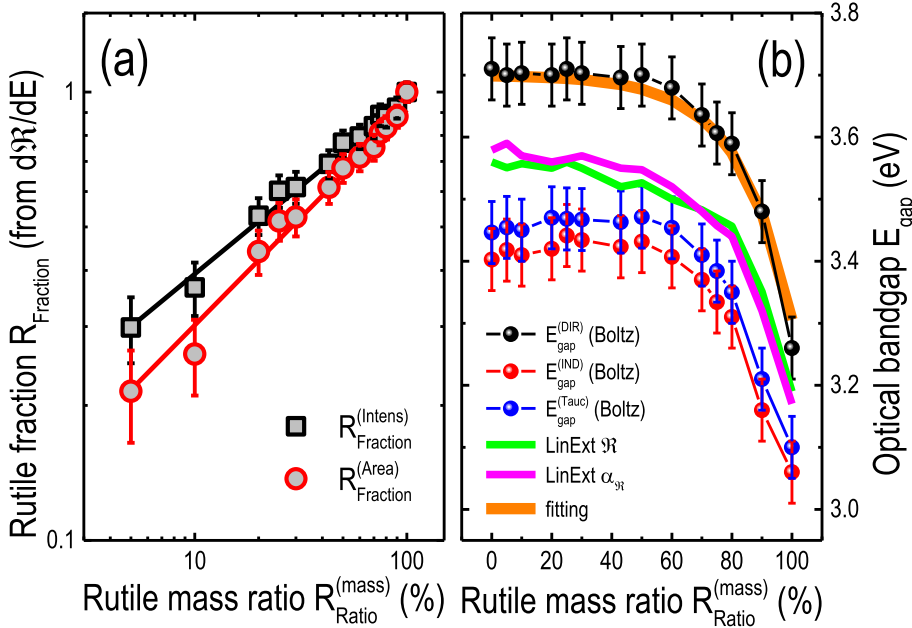

Fig. 2. (a) Rutile fraction $R_{Fraction}$ and (b) optical bandgap E_{gap} of A + R TiO$_2$ samples as a function of the rutile mass ratio $R_{Ratio}^{(mass)}$ ($= (R_{mass})/(R_{mass} + A_{mass})$). In (a) the straight lines indicate $R_{Fraction}$ as determined by the intensity signal [$R_{Fraction}^{(Intens)} = 0.16 \times (R_{Ratio}^{(mass)})^{0.39}$] and by the area signal [$R_{Fraction}^{(Area)} = 0.10 \times (R_{Ratio}^{(mass)})^{0.48}$]. E_{gap} was obtained by linear extrapolation of the $\Re$ (LinExt $\Re$) and $\Re$-related absorption (LinExt $\alpha_\Re$) curves; as well as by fitting $\alpha_\Re$ with a Boltzmann function rendering direct, indirect, and Tauc (amorphous-like) E_{gap} values [13]. In (b) "fitting" refers to $E_{gap} = E_{R0-gap}^{(meth)} - 0.0013 \cdot exp\left(\frac{R_{Ratio}^{(mass)}}{17.5}\right)$ with $E_{R0-gap}^{(meth)} = E_{R0-gap}^{(DIR)} = 3.71$. Similar results can be achieved by adopting $E_{R0-gap}^{(IND)} = 3.43$, $E_{R0-gap}^{(Tauc)} = 3.47$, $E_{R0-gap}^{(\Re)} = 3.55$, and $E_{R0-gap}^{(\alpha\Re)} = 3.58$. Error bars correspond to data dispersion due to different sets of measurements-analysis.

data processing (direct–indirect character and/or graphical representation) − that also depend on the main condition of TiO$_2$ (bulk, film, powder, or nanostructured) [10,11]. Intriguingly, the spreading of E_{gap}-related information also exists in the theoretical treatment of TiO$_2$ [12]. Apart from these issues, in this work, the E_{gap} of the A + R TiO$_2$ samples was obtained by considering different types of optical transitions (*i.e.*, direct, indirect, and amorphous-like), as well as by adopting various procedures.

Taking into account the composition of the samples (*i.e.*, essentially Ti and O atoms, but arranged according to different structures-phases), it seems obvious that the amount of rutile will influence the optical characteristics of the A + R TiO$_2$ samples. Therefore, both the d$\Re$/dE-related data and E_{gap} values were analyzed in view of the rutile mass ratio. In the first case, a rutile fraction ($R_{Fraction}$) was defined based on the intensity and area results provided by the Gaussian fittings of the d$\Re$/dE curves, or: $R_{Fraction}^{(Intens)} = (R_{Gauss}^{(Intens)})/(R_{Gauss}^{(Intens)} + A_{Gauss}^{(Intens)})$ and $R_{Fraction}^{(Area)} =$

$(R_{Gauss}^{(Area)})/(R_{Gauss}^{(Area)} + A_{Gauss}^{(Area)})$. In the later, the E_{gap} values were determined by the linear extrapolation of $\Re$ (and of its related absorption $\alpha\Re$), and according to the unified Boltzmann-based method − see [13] for details. Fig. 2 shows the results of $R_{Fraction}$ and E_{gap} as a function of the rutile mass ratio $R_{Ratio}^{(mass)}$. In Fig. 2(a) it is clear the relationship between the optical reflectance data ($R_{Fraction}$) and the rutile concentration ($R_{Ratio}^{(mass)}$) according to which it was possible to achieve $R_{Fraction}^{(Intens)} = 0.16 \times (R_{Ratio}^{(mass)})^{0.39}$ and $R_{Fraction}^{(Area)} = 0.10 \times (R_{Ratio}^{(mass)})^{0.48}$.

Even though this is not a linear relationship (mainly because of the inherent A- and R-related absorption processes), the optical reflectance data can be used to determine the amount of rutile with an (absolute) error < 5% − which is noteworthy considering the simplicity of the whole procedure.

Concerning the optical bandgaps [Fig. 2(b)], in spite of their different values (resulting from the various methods to estimate E_{gap})

there is also a connection between E_{gap} and $R_{Ratio}^{(mass)}$. Again, this is not a linear relationship, but its general behavior can be described by $E_{gap} = E_{R0-gap}^{(meth)} - 0.0013 \cdot exp\left(\frac{R_{Ratio}^{(mass)}}{17.5}\right)$ with the "R0-gap" values being dependent on the method to calculate E_{gap}, *i.e.*: $E_{R0-gap}^{(DIR)} = 3.71$, $E_{R0-gap}^{(IND)} = 3.43$, $E_{R0-gap}^{(Tauc)} = 3.47$, $E_{R0-gap}^{(\Re)} = 3.55$, and $E_{R0-gap}^{(\alpha\Re)} = 3.58$. Compared with the $d\Re/dE$-related results, the use of E_{gap} to evaluate the rutile amount involves a $\sim 10\%$ (absolute) error and, definitely, does not apply for $R_{Ratio}^{(mass)} \leq 60-70\%$.

In summary, this work reports (for the first time) the potential of optical reflectance spectroscopy to assess the amount of rutile R (or anatase A) phase in A + R mixed TiO_2 samples. The method is based on the reflectance spectra $\Re$, and it involves the use of reference curves that associate the $d\Re/dE$-related data to the amount of rutile — as determined by its relative mass ratio in A + R TiO_2 samples. The whole procedure is fast and straightforward and, in its present form, it is able to assess the amount of rutile (or anatase) phase with 5% of accuracy. The optical bandgap of the A + R TiO_2 samples was also investigated and correlated with the rutile mass ratio. In this case, however, the curves relating E_{gap} with $R_{Ratio}^{(mass)}$ are of limited (absolute error $\sim 10\%$) or no value (applicable only for $R_{Ratio}^{(mass)} \geq 60-70\%$).

Author statements

Antonio Ricardo Zanatta has conceived, conducted the whole experimental work (production, and optical reflectance measurements-analysis of the samples), and wrote/edited the manuscript.

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Declaration of Competing Interest

The author declares no conflicts of interest.

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