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Full Length Article

The temperature quenching of the cathodoluminescence bands in titanium dioxide

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ABSTRACT

The cathodoluminescence spectra of titanium dioxide (TiO_2) rutile powder have been measured under vacuum at a range of temperatures from 87 to 297 K. The bands with peaks centered at 3.41, 3.29, 2.63, 1.52, and 1.15 eV have been measured and the quenching of the bands with the observed temperatures. The peak intensities have been determined by deconvoluting the spectra with a series of fixed width Gaussian peaks and the relative intensities have been correlated with temperature quenching and an activation temperature for the bands has been calculated.

1. Introduction

Titanium dioxide powders are now being widely employed in various areas of science, technology and industry. They often perform the function of efficient photo-catalysts [1–3], such as pigments for thermal control coatings and reflection-proof covers for spacecraft [4,5]. Lately, many studies have been performed in order to explore their usability as photo converters for solar batteries [6,7]. Yet, they are most frequently applied as pigments in household dyes [8].

In the process of exploitation they are bound to be affected by the action of various radiation types, which leads to the formation of defects and absorption bands in the reflectance spectra. Therefore, the study of the point defects in titanium dioxide powders is significant for the advancement of science and technology.

In this respect, the absorption and luminescence spectra measured in a vacuum can specifically provide significant information. The vacuum registration forces gases, which are physically bound by sorption, to leave the powder's surface. This occurrence allows us to observe the bands of absorption and luminescence stipulated by the defects in the crystal lattice.

In the previous paper [9] a similar process in the titanium dioxide powders irradiated by the accelerated electrons was examined. The diffuse reflectance spectra (ρ_λ) were measured in situ before and after radiation influence. This research revealed that there are correlations between the changes in the intensity of the absorption bands created by the electron actions. The following examination of the cathodoluminescence (CL) at the temperature of liquid nitrogen and their registration in situ of titanium dioxide powders before and after electron treatment resulted in the demonstration of some peculiarities of their alterations [10]. The present paper describes the next stage of the aforementioned studies. It deals with the examination of the peculiarities of the transformations in the parameters of the CL bands under the actions of (1) the rutile powder temperature changes from 87 to 297 K; and (2) the spectra registration within a hard vacuum under strictly controlled conditions.

2. Methods

For our experiment we used TiO_2 (rutile) powders with a grain size of 240 nm and a specific surface area of 7.6 m^2/g. The experiment samples were produced by means of compression ($P=1$ Pa/cm^2) into metal cups with the dimensions with a height of 2 mm and a diameter of 24 mm which were placed onto the "Spectrum" position table [11].

The evacuation of the vacuum chamber was carried out by the aforementioned vacuum adsorption pump based on zeolites, and a high-vacuum diode type ion pump. The total gas pressure was 10^{-7} Torr. The mass spectrometric analysis showed that the main

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residual gases in such a system are: nitrogen, water, OH radicals, argon and hydrogen.

The excitation of the luminescence was carried by the electrons with an energy of 30 keV at a flow of 10^{13} sm^{-2} s^{-1}. The electron beam was focused on the study samples using magnetic lenses. The unevenness of the electron beam on the sample area which was measured by the slit diaphragm, did not exceed 5%. The continuous monitoring of the current of the electron beam during the recording of the luminescence spectra was maintained. To register the cathodoluminescence spectra, a photomultiplier tube in a region shorter than 1000 nm and a PbS photoresistor at longer wavelengths were used.

The surrounding stage and screen are cooled with liquid nitrogen. CL spectra were recorded in the range of 350–1200 nm in vacuum at $T=87$ K. Then, the heating of the stage was performed by an electric heater to increase the temperature. The spectra were recorded at each fixed temperature of 103, 148, 164, 173, 200, 213, 226, 258, 278 and 297 K.

3. Results and discussion

Several bands have been recorded in the CL spectra at a temperature value of 87 K. In the UV region a band has been recorded at 3.41 and 3.29 eV (Fig. 1); in the visible region a band has been recorded at 2.63 (Fig. 2); and in the near-IR region a couple bands have been recorded at 1.52 (Fig. 3) and 1.15 eV (Fig. 4). The bands recorded in the visible region are considered the most intensive. The band at 1.15 eV has not been recorded during previous experiments.

The increase in temperature value up to 297 K causes a decrease in the intensity of all the recorded bands. The correlation between the band intensity and the temperature has been approximated using the following function:

$$J_T = J_{87}\left[(1 - exp\,A(-E_a/KT)\right], \tag{1}$$

where E_a stands for activation energy, J_m is the band intensity at the definite temperature value, J_{87} is the band intensity at the temperature value of 87 K, and A is a constant.

Using logarithm (1) results in the following formula:

$$\ln(1-n) = A(-E_a/KT), \tag{2}$$

where $n=J_m/J_{87}$.

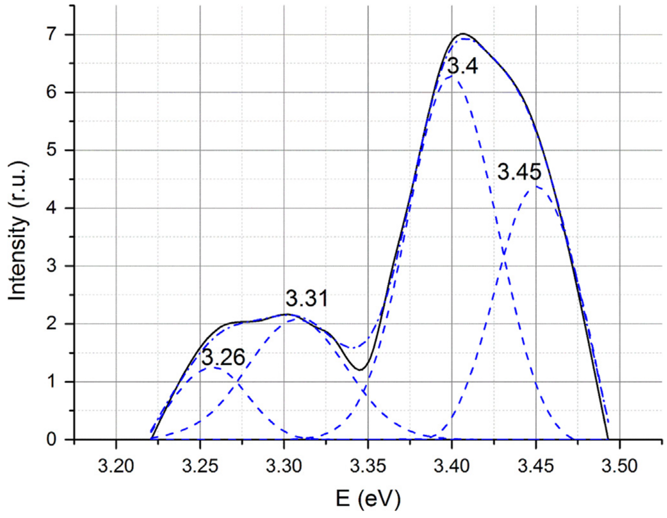

Fig. 1. The TiO_2 cathodoluminescence band in the UV region and its decomposition into the fundamental components.

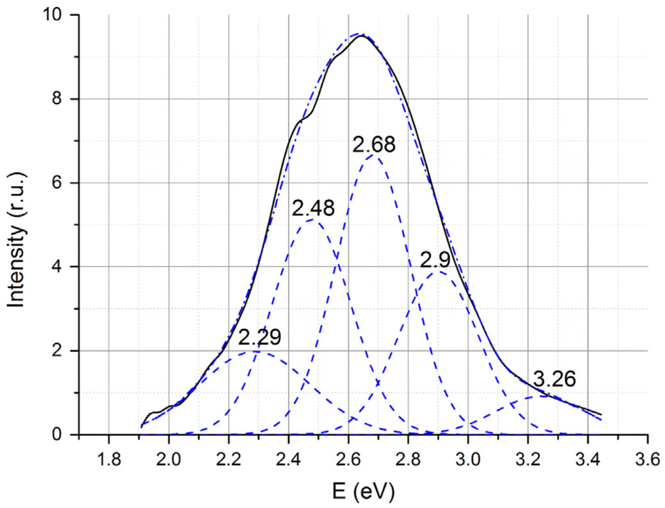

Fig. 2. The TiO_2 cathodoluminescence band in the visible region and its decomposition into the fundamental components.

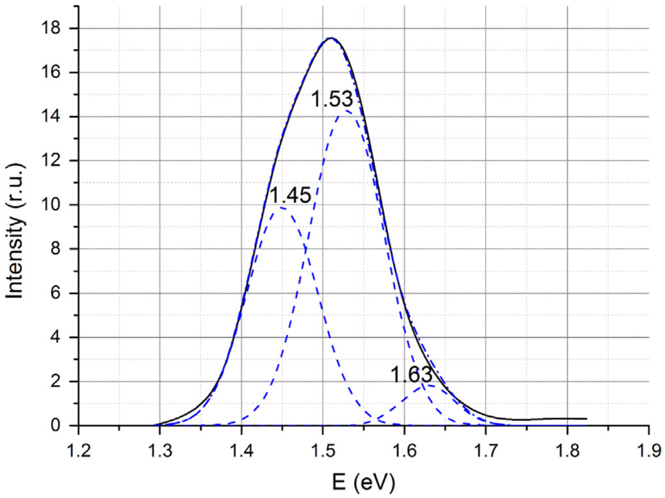

Fig. 3. The TiO_2 cathodoluminescence band in the near-IR region at 1.52 eV and its decomposition into the fundamental components.

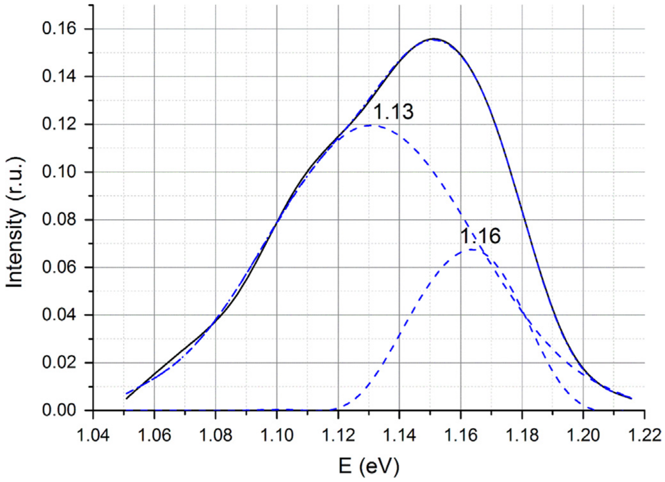

Fig. 4. The TiO_2 cathodoluminescence band in the near-IR region at 1.15 eV and its decomposition into the fundamental components.

The graphical representation of formula (2) allows us to define the value of activation energy for the processes that stipulate the decrease in the intensity of the absorption bands on the condition that the simultaneous temperature increases (Figs. 5 and 6).