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Optical property degradation of titanium dioxide micro- and nanopowders under irradiation

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A R T I C L E I N F O

A B S T R A C T

Diffuse reflection spectra and absorption spectra of titanium dioxide (anatase) micro- and nanopowders induced by exposure to 100 keV protons and electrons were analyzed at wavelengths between 250 and 2500 nm. It is established that the radiation stability of the nanopowders is higher than the micropowders in the absorption region $\lambda > 500$ nm for proton and electron exposure. This effect is caused by the high concentration of radiation defects in micropowders, which is associated with defects of interstitial titanium ions ($Ti_i^{...}$, $Ti_i^{....}$), titanium vacancies ($V_{Ti}^{'''}$, $V_{Ti}^{''''}$) and oxygen vacancies V_O^X.

1. Introduction

Titanium dioxide powders have the widest application among pigments as white coatings for spacecraft [1] because of their high stability under charged particle irradiation and solar radiation exposure. However, a number of defects and absorption centers are formed in these pigments during long-term spacecraft flight and are sufficient to decrease the spectral reflectance (ρ) in the UV, visible and near IR regions of the spectrum as well as increase the solar absorptance (a_s).

Therefore, the important issue is finding methods to improve the radiation stability of pigments and coatings. One approach to solving this problem is to use nanostructured materials as a pigment. According to reference [2], the radiation stability of nanoparticles depends on the balance of free energy from grain boundaries and point defects. From the study conducted, it was determined that zirconium dioxide nanopowders [3] have greater radiation stability than micropowders, although the opposite was determined for silicon dioxide dependence [4].

This effect is most likely because the silica nanoparticles have an amorphous structure. The main centers of the optical absorption are surface defects of non-bridging oxygen hole centers ($\equiv$Si—O$^{\cdot}$), peroxidation radicals ($\equiv$Si—OO$^{\cdot}$) and peroxide silicon ($\equiv$Si—O—O—Si$\equiv$), whereas zirconium dioxide nanoparticles with a crystalline structure includes the main types of radiation defects of oxygen vacancies and interstitial zirconium ions in the volume of the nanoparticles. The high specific surface area of nanoparticles leads to the overall proportion of radiation-induced defects in their volume but is usually smaller in value than that of the microparticles. These assumptions require further research on the radiation stability of other wide-gap oxides, particularly titanium dioxide.

It is well known that radiation stability is the ability of materials to maintain their initial chemical composition, structure and properties during and after exposure to ionizing radiation. As a result of the radiation-induced processes, ions and free electrons can participate in complex chains of physical and chemical transformations that lead to radiation defects as well cause a change in optical, electrical and other properties. The formation of color centers results in changes in the optical properties.

The absorption bands of the donor-type defects for TiO_2 are near the following values of the energy quanta (in eV): in the Kroger–Vink notation, the interstitial ions titanium Ti_i – 3.08, $Ti_i^{\cdot}$ – 2.48, $Ti_i^{...}$ – 2.22 or 1.47–1.56, and $Ti_i^{....}$ – 1.71, and the oxygen vacancies are V_O – 2.53 or 1.78, $V_O^{\cdot}$ – 2.11 or 1.18 and V_O^X – 0.877. The acceptor defects include the following: interstitial oxygen O_i' – 2.69, O_i'' – 1.95 and titanium vacancies $V_{Ti}^{''''}$ – 1.71 or 1.44, $V_{Ti}^{'''}$ – 1.15 or 0.82. To determine the point defect, a computational method was used to integrate the ab initio electronic structure

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and thermodynamic calculations [5–8] in addition to visible absorption and reflectance spectroscopy [9–11]. The absorption in the near-infrared region is usually caused by various vibrations of OH groups (0.87, 0.64 and 0.55 eV) [12].

The purpose of this study is to perform a comparative study of diffuse reflectance spectra of micro- and nanopowders of titanium dioxide and their changes following irradiation by protons and electrons.

2. Experiment

The objects of research were micro- and nanopowders of titanium dioxide with 99.8% purity, purchased from the company Aladdin Chemistry. The average particle size of the micropowder was 500–600 nm, while the nanopowder was 40–50 nm as measured by a Horiba LA-920 particle size distribution analyzer. An X-ray diffraction (XRD) analysis was performed using the X-ray diffractometer Philips X'Pert PRO MRD ($V = 40$ kV, $I = 40$ mA, Cu Kα = 1.5405) using the Debye–Scherrer method. The phase composition and unit cell parameters were calculated using the MDI Jade software package.

To determine the radiation stability of the micro- and nanopowders, samples were prepared by pressing under 1 MPa of pressure for 2 min to form discs on an aluminum substrate, each with a diameter of 17 mm and a height of 4 mm. The reflective spectra of the samples were measured using a Perkin Elmer Lambda 950 spectrophotometer with a scanning rate of 5 nm/s and wavelengths between 250 and 2500 nm. The samples were irradiated with protons and electrons under identical conditions: the particle energy was 100 keV, the fluence was 5×10^{15} cm^{-2}, the flux density was 1×10^{12} cm^{-2} s^{-1}, and a vacuum was maintained at 2.5×10^{-4} Pa.

3. Experimental results

It is established from the obtained XRD spectra (Fig. 1) that the micro- and nanopowders of titanium dioxide with anatase structural type I41/amd have the cell parameters of the TiO$_2$ micropowder, which are $a = 3.799 \pm 0.002$ Å and $c = 9.756 \pm 0.003$ Å. The

parameter a of the nanopowder increased to 4.069 ± 0.002 Å, but the parameter c decreased to 9.452 ± 0.003 Å.

The edge of the main absorption peaks for both of the TiO$_2$ powders nearly coincides as observed in the reflection spectra of the initial micro- and nanopowders (Fig. 2A). The band gap (E_g) is defined as the intersection point of the horizontal axis and the tangent line of a sharp increase of the reflectance in the UV region (Fig. 2B). Therefore, the resultant is TiO$_2$ from micropowder sand nanopowders with band gaps of 3.48 eV and 3.54 eV, respectively. The difference between the E_g values is caused by the difference between the crystal lattice constants of these powders. The values of E_g are slightly higher than the band gap values of titanium dioxide films with the anatase lattice (E_g = 3.46 eV) [13,14].

The reflectance of the nanopowder is higher than the micropowder in the wavelength region from the edge of the main absorption peak of 1750 nm. In the region from 1750 to 2500 nm, it is the opposite; the reflectance of the nanopowder is less than that of the micropowder. The region from 200 to 2500 nm can be divided into three parts. The first part before 500 nm is characterized by a lower value of the reflectance for the nanopowder, but the second part from 500 to 1750 nm has larger values. The third part with $\lambda \geqslant 1750$ nm has lower values of the reflectance compared to the micropowder.

The lower reflectance at the first part of the spectrum can be ascribed to a higher concentration of lattice defects in the surface layer of the nanopowder relative to the micropowder. Therefore, the intensity of the absorption bands increases, and as a result, the reflectivity decreases. The larger value of the reflectance at the second part of the nanopowder spectrum ρ_λ is determined by the large scattering of light caused by the smaller grain sizes [15]. The absorption at the third part of the spectra is caused by free electrons and chemisorbed gases [16]. The transitions of the free electrons in continuous levels in the conduction band determine the power dependency of the absorption coefficient on the wavelength. Such dependences clearly registered for the various semiconductor compounds [16]. Another component for the third part of the ρ_λ spectra are the bands of chemisorbed gases at 1430, 1780, 1940 and 2270 nm [12].

From Figs. 3 and 4, it is observed that the absorption bands in the UV and near-IR regions of the powder were induced by proton
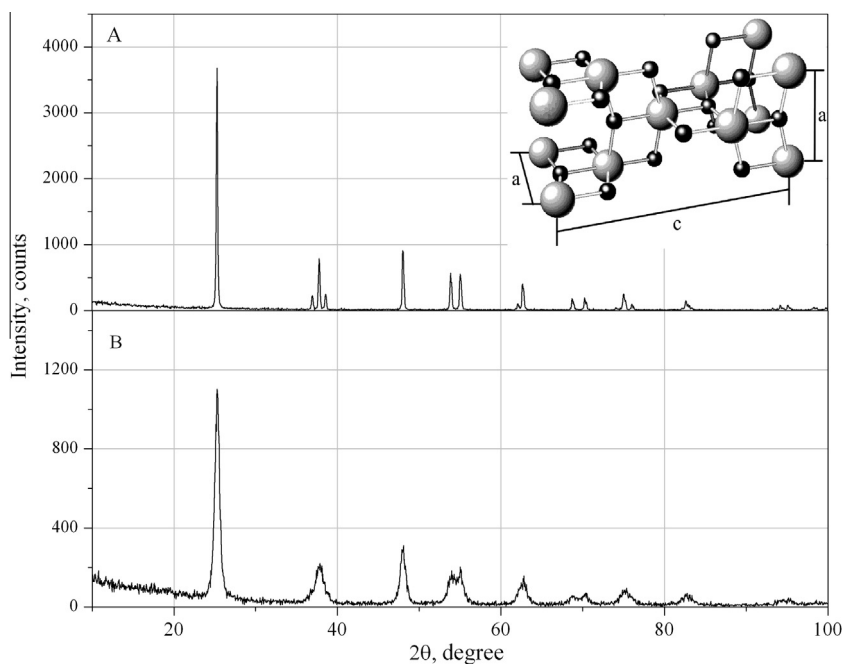

Fig. 1. XRD of titanium dioxide micro- (A) and nanopowders (B).