MICRO-RAMAN SPECTROSCOPY OF TiO_2

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Titanium dioxide has been investigated extensively in recent years because of its many applications in photoelectrical cells [1, 2], in photocatalyst [3], dye-sensitized solar cell [4], gas sensor [5]. Titanium oxide ceramics has been self-cleaning components and biomaterials [6-9].

Using special treatment of noon-conductive TiO_2 ceramics it becomes conductive. In different temperatures vacuum treated titanium oxide ceramic samples exhibit n-type conductivity

The present work describes the results of investigation of TiO_2 phases transform depending of temperature and treated atmosphere by micro-Raman spectroscopy. Among different experimental techniques the micro-Raman spectroscopy is a useful tool to study non-homogeneous samples. It combines the ability to scan a sample with micro-level lateral resolution and the possibility to distinguish different Raman-active phases, thus providing the information on phases distribution across the sample.

TiO_2 containing samples were prepared using dry extrusion technology. Extrusion mass consisted of anatase (TiO_2) and cellulose containing additives. Obtained green bodies (10 mm in diameter and 30 mm in length) were heated at 1150 °C with 5 °C/min heating rate and 2h dwell time. Samples were further treated in vacuum ($6.6 \cdot 10^{-3}$ Pa) in temperatures 1200°C, 1225 ºC, 1250 ºC, 1275 ºC, 1287 ºC, 1300 ºC and 1350 ºC with 7 °C/min heating rate and 1h dwell time. After sintering the samples were cut into 20 mm long rods. Ends of the samples were polished with SiC paper in the sequence of 280, 1500, 2000 grit and cleaned with ethanol.

Raman spectra were collected at room temperature using a confocal microscope with spectrometer "Nanofinder-S" (SOLAR TII, Ltd.). The “Nanofinder-S” system consists of an inverted Nikon ECLIPSE TE2000-S optical microscope connected simultaneously to a laser confocal microscope unit with Hamamatsu R928 photomultiplier tube (PMT) and to a monochromator-spectrograph (SOLAR TII, Ltd., Model MS5004i, 520 mm focal length) with attached Hamamatsu R928 PMT detector and Peltier-cooled back-thinned CCD camera (ProScan HS-101H, 1024×58 pixels). The colour video CCD camera (Kappa DX20H) is used for optical image detection. All measurements were performed through Nikon Plan Fluor 40x (NA=0.75) optical objective. The Raman spectra were excited by a He-Cd laser (441.6 nm, 50 mW cw power) and dispersed by 600 or 1800 grooves/mm diffraction grating. The elastic component of the laser light was eliminated by the edge filter (Omega, 441.6AELP-GP). The spectrum scattering detection region was from 200 cm^{-1} to 3500 cm^{-1}.

Raman spectra of anatase were measured at room temperature through 50× microscope objective using Renishaw inVia micro-Raman spectrometer equipped with argon laser (514.5 nm, max cw power P_{ex}=10 mW). The spectral signal was dispersed by the 2400 grooves/mm grating onto Peltier-cooled (-60°C) CCD detector.

Raman spectrum for anatase at room temperature consists of following allowed bands (figure 1:left panel) 144 cm^{-1} (E_g), 197 cm^{-1} (E_g), 399 cm^{-1}(B1g), 513 cm^{-1} (A1g), 519 cm^{-1} (B1g), and 639 cm^{-1}.

the Raman spectrum of rutile crystal treatment, exhibiting dominant peaks at 140, 235, 446, 610, and 82 cm^{-1}, which are assigned to the five Raman active modes of rutile single crystal.

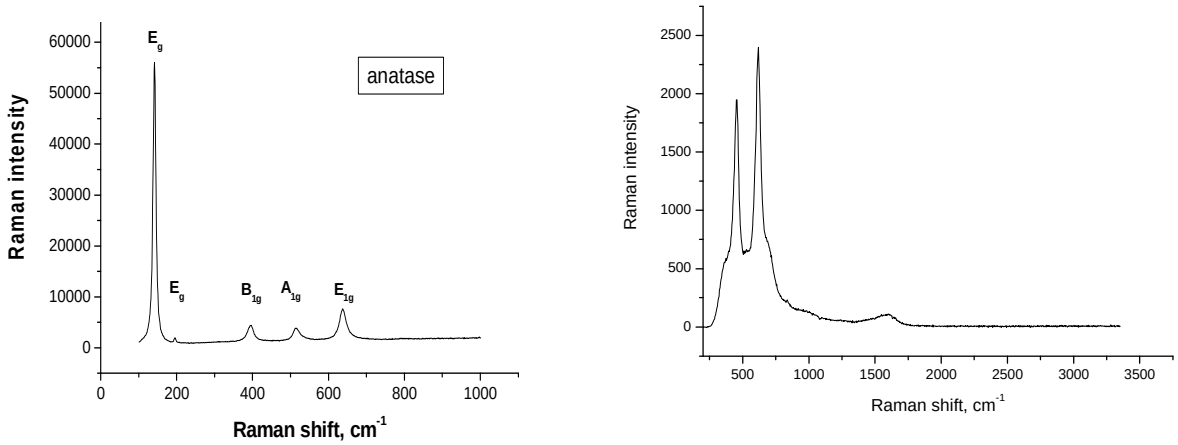


Figure 1.Raman spectra TiO_2 before treatment Left panel: Room temperature (T=300 K) Raman spectra of the anatase-TiO_2 .. Right panel: Room temperature (T=300 K) Raman spectra of the rutile-TiO_2 before treatment. The vibration mode symmetries of the anatase and rutile are indicated.

In vacuum treated samples changed the colour to black. XRD patterns of all samples treated in vacuum showed presence of rutile crystalline structure. Anatase specific crystalline structure was not found.XRD patterns of all samples treated in vacuum showed presence of rutile crystalline

Morphology. To compare morphology of the raw materials and obtained samples SEM was used. Particle size and shape for both TiO_2 anatase and rutile are nearly the same. The particles are round shaped and agglomerated. All samples sintered in air atmosphere shoved the same grain size and microstructure. Samples sintered in vacuum atmosphere have average grain size about 100 мm while samples sintered in air atmosphere have 10 times smaller grains, pointing that vacuum atmosphere is promotable for grain growth than air one [10,11].

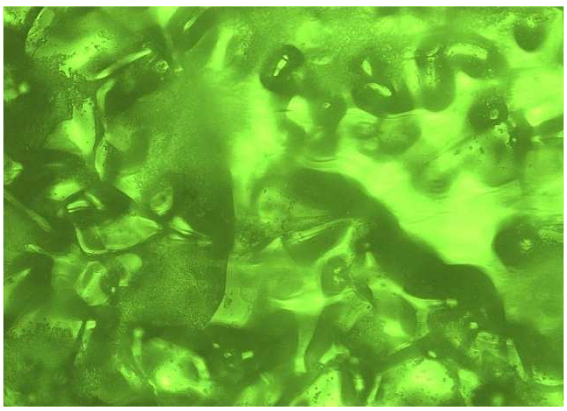


Figure 2. Optical image of TiO_2 after treatment.

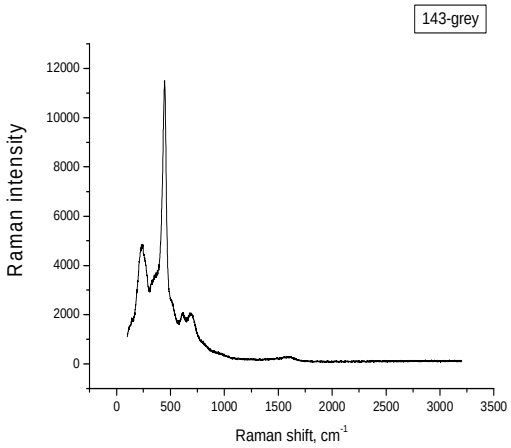
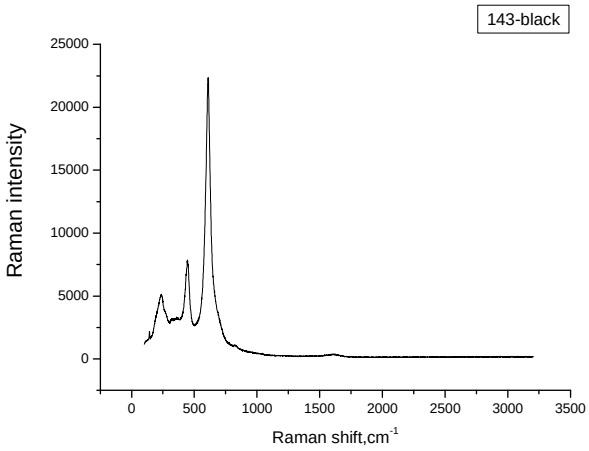


Figure 3. Raman spectra of TiO2 (grey)



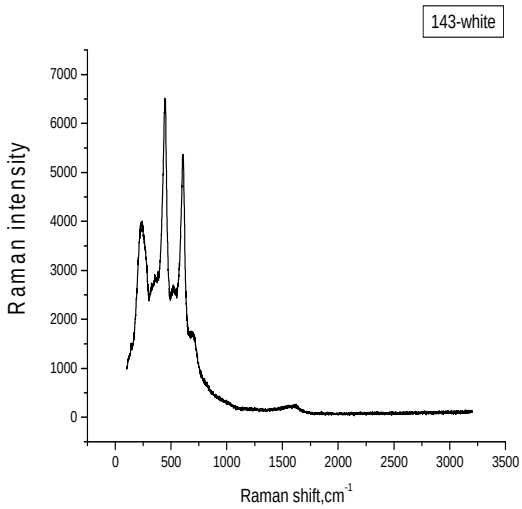


Figure 2. Raman spectra of TiO2 black and white phase.

Confocal micro-Ramanwere used to probe the phase composition of TiO2 the raw material and the samples sintered in air and vacuum.

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