

RAMAN SPECTROSCOPIC STUDY OF SHOCK-INDUCED PHASE TRANSFORMATIONS OF NANOCRYSTALLINE ANATASE TiO₂

Shulga Y.M., Matyushenko D.V., Golyshv A.A., Shakhray D.V., Molodets A.M., Kurkin E.N., Domashnev I.A.

Institute of Problems of Chemical Physics RAS,
av. acad. Semenov 1, Chernogolovka Moscow reg., 142432 Russia.

Introduction

Titanium dioxides TiO₂ are interesting because its important technological application in photocatalysis, photochemical solar cells, optoelectronic devices, chemical sensors, and dielectric materials of ultra fine thin-film capacitors. New peculiarities can be found in any materials then ratio of surface atoms to volume atoms in the crystalline units is increased.

TiO₂ can exist in several crystallographic phases. Two tetragonal phases (anatase - *P4/mmm* and rutile - *I4₁/amd*) are more known. Anatase transforms in rutile at approximately 800 °C. The transition temperature will be diminished in the case of decreasing of particle sizes or adding of catalysts. Anatase transforms first at static pressure 2-5 GPa to a columbite (orthorhombic PbO₂ type - *Pbcn*), and then to a polymorph isostructural to the baddeleyite structure (monoclinic ZrO₂ - *P2₁/c*) at pressure more than 10 GPa. These conversations are take place if the pressure applied at room temperature. Rutile transforms to monoclinic structure at $P \approx 12$ GPa. Orthorhombic phase found after decompression for booth types of initial materials comprised of sufficiently large particles (see, for example [1-3]).

Titanium dioxides are not investigated under high dynamic pressures. Shock waves acts as usual short time. Characteristic time is equal to microsecond. High-speed deformation is also inherent in this case. It is obviously that other products can be formed under these conditions in compare with those in conditions of static pressure. The coal of this work is to study of products of polymorph transformations of nonosized anatase after shock wave compression. Raman spectroscopy was used as main method of investigation because it allows to establish not only phase states but also to control size of nanoparticles (see below).

Experimental

Two powder TiO₂ samples were choused for investigation. Sample 1 was synthesized from TiCl₄ by sol-gel method. Sample 2 was available from Aldrich (cataloged No 637254). Raman

spectra were registered with help of NXT FT-Raman 9650 spectrometer ($\lambda = 976$ nm).

The spectra of the initial samples under study are presented in Fig.1. It is shown that the spectra differ not at all from each other.

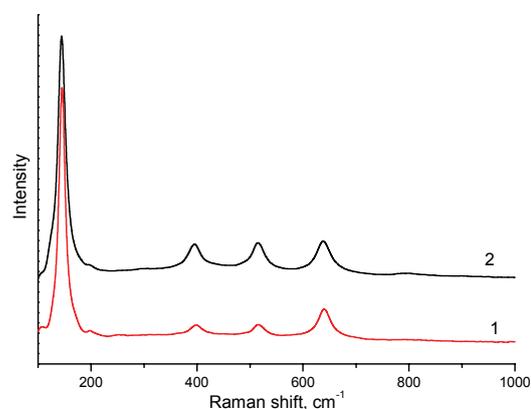


Fig. 1. Raman spectra for both initial samples of TiO₂. Number of spectrum corresponds to number of sample (see text).

As it is evident throughout the literature one can shown in Raman spectra of anatase TiO₂ three E_g peaks, which are placed at 144, 197, and 969 cm⁻¹ (in work [1] these peaks were denoted as E_g(1), E_g(2), and E_g(3) correspondently), two B_{1g} (399 and 519 cm⁻¹), and A_{1g} peak (513 cm⁻¹). Peaks at 513 and 519 cm⁻¹ will be resolved only at low temperature [4], and E_g(2) peak has very low intensity. In our case we see in the spectra all peaks, which are characteristic for Raman spectrum of anatase at room temperature. In accordance with the relationship between position of E_g(1) and size of anatase particles [5] average sizes 22 and 25 nm correspond to sample 1 and 2 correspondently. Hence the sizes of particles that make up the samples are practically the same in limits of accuracy of experimental relationship [5].

Shock wave treatment of the samples was performed with help of special equipment, which described in details in work [6]. Before treatment powder samples were compacted in the pellets with diameter 10 mm and high 0.9 mm. In the case of sample 1 density was equal to 2.34(2) g/cm³. At

the same conditions of compacting the density of samplthae 2 was equal to $1.94(5) \text{ g/cm}^3$.

Results and discussion

After shock treatment sample 1 converted into a columbite in accordance with literature overview. The fine structure of the spectrum obtained by us (Fig.2) is coincident with that columbite which was made in result of static pressure treatment [2]. Here we present the peak position in our spectra because such data are not found in literature: 152.4, 173.9, 285.2, 315.6, 339.7, 356.8, 426.3, 532.5, 568.5 and 604.7 cm^{-1} .

The sample 2 is turned to gray powder in result of similar treatment. Elemental analysis is found admixture of cooper atoms (several mass. %) Raman spectrum of the sample has a very low intensity (Fig.2). Diminishing of the intensity corresponds to amorphoization of the sample [7]. Nevneverless long time collection of the spectrum leads to appear two peaks (443.4 and 604.6 cm^{-1}), which can be attributed to E_g and A peaks of nanosized rutile. As it follows from presented in [3] dependence of A1g peak position on size of rutile particle sizes in our sample this parameter is equal to 5 nm.

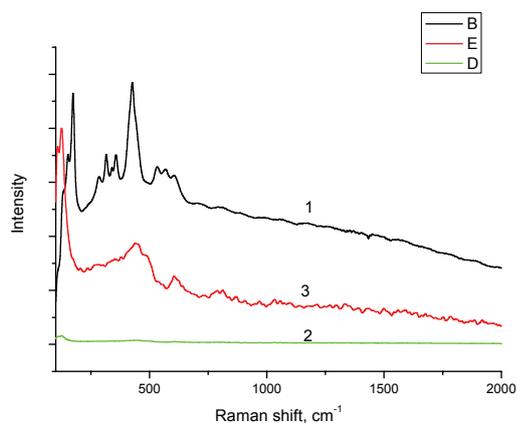


Fig.2. Raman spectra for the samples of TiO_2 after shock wave treatment. Number of spectrum corresponds to number of sample (see text). Spectrum 3 corresponds to spectrum 2 for which scale of intensity multiply by 25.

Thus our investigation are shown that the density of the pellet has a is important for anatase conversion in shock wave compression. It is known (see for example [8]), that decreasing in start density of the sample leads to increasing its temperature at this treatment. It can be thing that more high temperature in the case of sample2 leads to transform of initial nanosized anatase not in columbite but in amorphous phase with admixture of rutile with very small particle size (5 nm).The influence of temperature factor on conversation of nanosised anatase starting material in shock wave conversation will be studied in next our work.

References

1. Swamy V., Kuznetsov A., Dubrovinsky L. S., Caruso R.A., Shchukin D. G., Muddle B. C., Phys. Rev. B **71**, 184302 (2005).
2. Swamy V., Kuznetsov A., Dubrovinsky L. S., McMillan P. F., Prakapenka V.B., Shen G., Muddle B. C., Phys. Rev. Lett. **96**, 135702 (2006).
3. Swamy V. Phys. Rev. B **77**, 195414 (2008).
4. Mikami M., Nakamura S., Kitao O., Arakawa H., Phys. Rev. B 2002. V.66. P.155213.
5. Shulga Y.M., Matyushenko D.V., Kabackov E.N., Kolesnikoba A.M., Kurkin E.N., Domashnev I.A., Brichkin S.B.// Pis'ma JTP (in print).
6. Kanel G.I., Molodets A.M., Vorob'ev A.A. // FGV.1974. T. 10. №6, C. 884-891.
7. Ma W., Lu Z., Zhang M.// Appl. Phys.A. **66**, 621 (1998).
8. Zel'dovich Ya.B., Rayzer Yu.P. Shock Wave Physics and high-temperatures hydrodynamic ivents M: Nauka, 1966.