
TEMPERATURE DEPENDENCE OF PHOSPHORESCENCE FOR TITANIUM DIOXIDE - BENZOPHENONE HETEROGENEOUS SYSTEM

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The heterogeneous two-component system on the basis of titanium dioxide TiO₂ (anatase structure) nanoparticles with Fe-modified surface, loaded into benzophenone (BP), has been studied in the temperature range 4.2-180 K by the phosphorescence method. The presence of two BP spectral band series with different temperature dependences of their spectral parameters has been observed. The analysis of the obtained data allowed us to draw conclusion about a simultaneous realization of BP two structural modifications, namely amorphous and crystalline phases, in the studied sample. The disordered amorphous structure is formed in thin (less than 0.05-0.1 μm) near-surface layers of BP and results from destruction of long-range ordering in this compound due to the influence of the strongly defective TiO₂ surface.

Introduction

In recent years, great attention has been focused on titanium dioxide (TD) materials because they exhibit a variety of controllable electronic and optical properties and have extensive applications. TD is proved to be a good and perspective active component for different types of catalysts and photocatalysts. There are a number of publications describing its role in the destruction processes of many organic compounds. In comparison with other semiconductor catalysts, TiO₂ is biologically and chemically inert, stable to photodegradation, and also relatively cheap [1-3].

Experimental results showed that the synthesis techniques and the processing conditions have a strong influence on the microstructure, electronic properties, and lattice dynamics of TiO₂ powders. One of the numerous ways to modify these materials is to adsorb doping atoms of various valences on their surface or to incorporate them into the crystalline structure [4, 5]. Both these procedures lead to changes in the electron-donor properties of the TiO₂ surface and to considerable changes in the photocatalytic activity. It

has been demonstrated [6-8] that TiO₂ photocatalytic activity increases if the concentration of doping atoms does not exceed 0.2-0.5% mas. Adatoms can result in the appearance of new states in the energy gap of a TiO₂ bulk material. For instance, the presence of coordinationally unsaturated Fe-atoms on a TiO₂ particle surface leads to new single electron levels, which decrease the frequency of the optical transition during electromagnetic irradiation, thus increasing the catalyst photoactivity [9].

Many processes, which play a significant role in catalysis and photocatalysis, occur on the solid-state surface or in the near-surface layers. Therefore, investigations of the solid surface state, the nature and concentration of different surface active centers and defects, and possibility of controlled modification of these parameters in order to create materials with desirable properties are of great importance. On the other hand, solid substrate is known to affect its molecular surrounding, first of all, the structure and properties of the near-surface layers. In some cases, organic substances with anisotropic molecules can even form orientationally ordered thin layers near a lyophilic surface similar to nematic liquid crystals [10]. The mentioned effects are mainly caused by intermolecular interactions between the molecules from the environment and active centers on the solid surface.

Heterogeneous systems of inorganic-organic type, that have the enormous area of the solid surface, and, consequently, a large phase separation boundary, are found to be suitable objects for the investigations of the solid surface effect on the structure and properties of the surrounding organic substance, molecular interactions, as well as the influence of a surface state and treatment on the near-surface layers.

In this work, the two-component heterogeneous system based on TiO₂ (anatase structure) nanocrystallites with Fe-modified surface and

benzophenone (C_6H_5)₂CO as an organic medium has been studied by the phosphorescence method. Pure BP has some interesting properties (considerable piezoelectric effect, high quantum yield of phosphorescence, and good photochemical activity in hydrogen-containing solvents). Electronic spectra of its different structural modifications have been investigated before [11–13]. BP exists in three crystal modifications, one stable and two unstable, with melting points at 322, 301, and 296 K, correspondingly [14]. The amorphous glass-like phase (χ -modification) is formed after abrupt cooling of the benzophenone melt and is observed below $T = 216$ K [15]. Luminescence spectra of polycrystalline TiO_2 have been also presented in literature [16]. It is worth mentioning that our experimental data on luminescence of bulk BP and TD powders are in a good agreement with the literature data.

Experimental

BP crystals (C_6H_5)₂CO were obtained by the multiple zone melting method (up to 40 zones). Its purity was controlled by the presence of excitation phosphorescence.

Titanium dioxide is known to exist in three crystalline modifications: rutile (tetragonal), brookite (orthorhombic) and anatase (tetragonal). For our experiments, we prepared TiO_2 powders with particles of the anatase crystal structure, which have been produced with a high degree of chemical purity (the amount of coloring admixtures such as Co, Cr, Cu, Ni, Mn, and V does not exceed $1 \cdot 10^{-5}$ % mas.) [17]. The TiO_2 preparation method included thermal hydrolysis of titanium tetrachloride $TiCl_4$ initially digested in hydrochloric acid HCl and then diluted in distilled water [18]. The synthesis was carried out under normal pressure and a temperature of 373 K in the presence of specially prepared titanium nuclei, which were added to control the process of crystal growth. In order to obtain a Fe-modified and, as a result, more defective TiO_2 surface, an iron chloride $FeCl_3$ solution was added during the hydrolysis process. The quantity and concentration of dopants included have been estimated by taking into account the known amounts of initial substances. Fe cations were added as 0.2–0.5% mas. of TiO_2 ending product mass. This process was controlled by filtrate analysis in the presence of the corresponding cations. Produced TiO_2 particles had almost a spherical shape with a typical size of 10–30 μm in diameter and consisted of nanocrystallite aggregates. Their anatase crystal structure has been confirmed by X-ray analysis (DRON-2, $Cu K\alpha$ radiation). The TD⁻BP heterogeneous system has been obtained by loading TiO_2

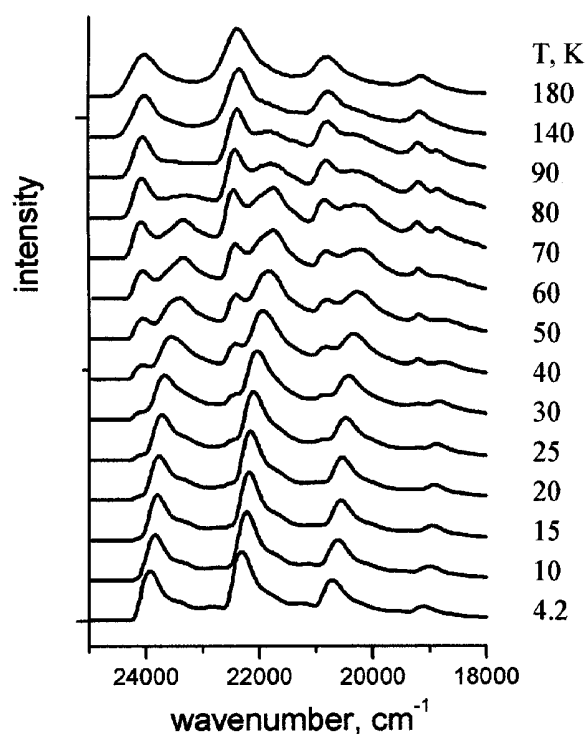


Fig. 1. Phosphorescence spectra of TD⁻BP heterogeneous system measured in the temperature range of 4.2–180 K

particles into the BP melt, subsequent mixing and cooling down to room temperature.

The phosphorescence spectra of the TD⁻BP system have been measured in the temperature interval 4.2–180 K and the spectral range 28000 – 16000 cm^{-1} . We used an MPF-4 Hitachi spectrofluorimeter for recording the phosphorescence spectra. The excitation line was $\lambda_{exc} = 360$ nm. Low-temperature measurements were carried out in a helium cryostat with a temperature control system with accuracy of not worse than ± 0.1 K.

Results and discussion

The phosphorescence spectra of the TD⁻BP heterogeneous system measured in the temperature range 4.2–180 K are presented in Fig. 1. At $T = 4.2$ K, a series of intense bands ($\nu_{0-0} = 33923$ cm^{-1}) is observed in the spectra, forming a progression with a thrice-repeated frequency interval of ~ 1600 cm^{-1} , which is characteristic of molecular vibrations of C=O carbonyl groups in the ground state of BP molecules (band series I). When the temperature increases, these bands gradually shift as a whole towards longer-wavelengths. At $T = 60 \div 70$ K, the shift reach its maximum value of ~ 600 cm^{-1} . At further heating, bands of series I

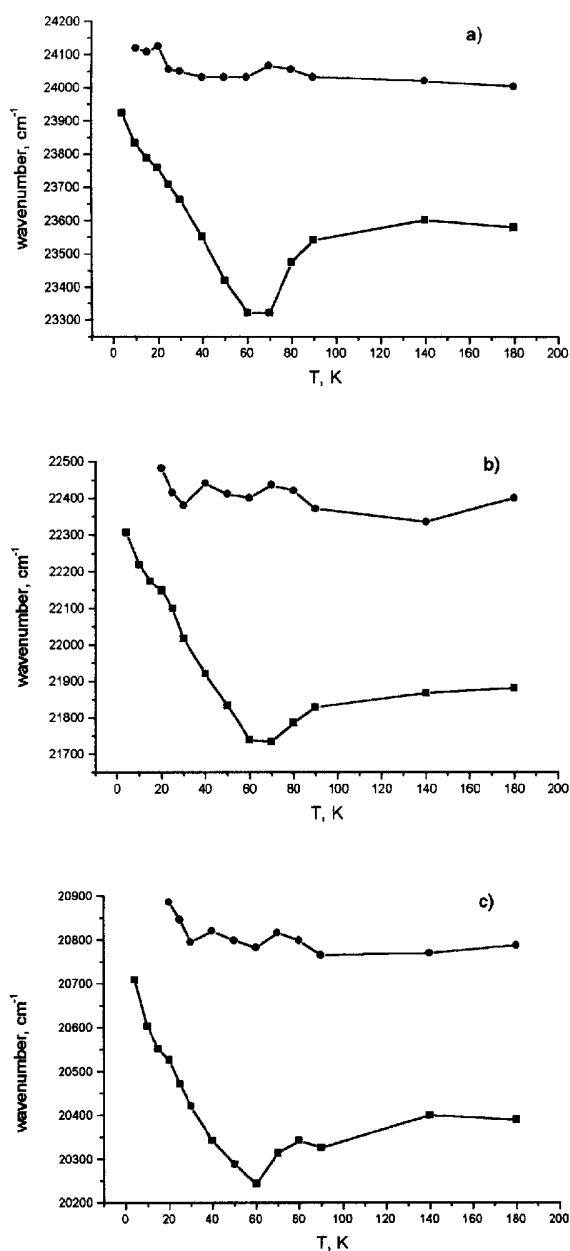


Fig. 2. Temperature dependence of BP phosphorescence band frequencies in the case of series I (solid squares), series II (solid points): a) 0^0_0 band; j) $0^-_0 + \nu(\text{C}=\text{O})$; e) $0^-_0 + \nu(\text{C}=\text{O})$ at heating

shift towards the opposite side, to shorter wavelengths. The temperature dependences of peak positions for three most intense bands of series I are shown in Fig.2 starting from the 0^0_0 transition band. In addition it should be noted that the luminescence intensity of this series significantly decreases with increase in temperature.

At the same time with the temperature evolution of series I, a new series of phosphorescence bands with $\nu_{0^-_0} = 24119 \text{ cm}^{-1}$ and the same vibrational

frequencies (series II) appears at $T = 10 \text{ K}$. At higher temperatures, these bands are observed more clearly, and their relative intensity essentially increases (see Fig. 1). When the temperature reaches 180 K, the phosphorescence spectrum consists only of series II bands, while the series I is not practically observed at all. It is worth mentioning that when the temperature increases, the peak positions of series II bands slightly shift (by up to $\sim 100 \text{ cm}^{-1}$) towards longer wavelengths (Fig.2). The fact that the phosphorescence spectra of amorphous and crystalline BP modifications are not well resolved at $T = 4.2 \pm 10 \text{ K}$ results from a strong overlap of their 0^0_0 bands. The values of peak positions and half-widths for these bands are 23923 and 400 cm^{-1} , 24119 and 182 cm^{-1} , correspondingly, at these temperatures.

In addition to the above-mentioned most intense series (I and II) of bands, in the phosphorescence spectra of the TD-BP system, a set of significantly less intense bands with frequency intervals of $\sim 1600 \text{ cm}^{-1}$ can be detected. These additional series can result from the presence of different type defects in our sample. Below we will take into account only the phosphorescence bands of series I and II. When analyzing the temperature shifts and changes in the relative intensity of spectral bands, the region of pure electron (0^0_0) and the first electron-vibration transitions is the most suitable.

As was shown [19], the phosphorescence spectrum of bulk amorphous BP also demonstrates a similar temperature behavior, being red-shifted as a whole. When the temperature increases up to $90\text{--}100 \text{ K}$, the peak position of the $\nu_{0^-_0}$ band centered at about 23700 cm^{-1} at $T = 4.2 \text{ K}$ shifts towards longer wavelengths by 370 cm^{-1} . At a further heating up to 220 K , the peak position of this band shifts towards the opposite, i. e. short-wavelength, side again by 370 cm^{-1} . Such a temperature behavior of the phosphorescence spectra of pure amorphous BP has been explained on the basis of the so-called spectral diffusion concept for triple excitations in the case of inhomogeneous broadening of bands [20] and by the significant temperature dependence of migration efficiency of the electron excitation energy in disordered media [21]. The phosphorescence bands of amorphous BP are non-uniformly broadened and have the Gaussian distribution. This is mainly due non-equivalent local fields, which affect each emitting molecule and create a quasicontinuous set of electron states, and to the significant amount of BP molecule configurations resulted from wide choices for changes in bend and torsion angles between BP phenyl rings. Energy migration considerably depends on temperature. At a temperature increasing from 4.2 to 100 K , the diffusion coefficient for amorphous BP

increases from $8 \cdot 10^{-11}$ to $1.2 \cdot 10^{-8} \text{ cm}^2 \text{ s}^{-1}$ [21]. This leads to more effective migration of triple excitations and, consequently, to the primary occupancy of low-energy levels in the frame of a broadened contour. Experimentally, a long-wavelength shift of phosphorescence spectra is observed. At a further temperature increasing, thermal activation equalizes the energy loss, and then the higher energy states become occupied. At these temperatures, we observe a blue shift of BP phosphorescence spectra. As an example, Fig.3 shows some phosphorescence spectra of the bulk amorphous BP in the corresponding temperature range.

We observed similar regularities, as those mentioned before, for the band series I in the phosphorescence spectra of the TD-BP heterogeneous system. This allows us to assign the series to the presence of BP amorphous phase the sample. Differences in the values of the shuttle-like shift and its temperature dependence, observed in the phosphorescence spectra of the TD-BP heterogeneous system, as compared to the spectra of bulk amorphous BP, can be ascribed to the specific influence of the nanoparticle surface on the adjacent layers of the organic medium, which is mainly a result of interactions between BP molecules and active centers of the solid surface. Loading of TD particles into BP leads to the even higher degree of BP disordering and, as a consequence, to greater variety in conformations realized for BP molecules. In this case, local fields, in which BP molecules are, also strongly change (due to changes in molecular surroundings, polarizing influence of cations on the TiO_2 surface, etc.). These effects result in changes of electron-vibration states of BP molecules, which leads to a broader set of occupied energy levels. Thus, we observe the mentioned differences in values of the 0^0 frequency and its maximal temperature shift in BP phosphorescence bands of the TD-BP heterogeneous system as compared to the bulk BP.

In order to explain an abrupt decrease in the phosphorescence quantum yield of the series I bands observed for the TD-BP system at temperatures above $T = 70 \text{ K}$, we used the data and conclusions made during the investigations of the temperature effects on the spectral-kinetic characteristics of phosphorescence in the thin films of amorphous BP [22]. It has been shown that the luminescence quenching rate in the case of thin films is greater than in the case of bulk samples. At the same time, the luminescence quenching rate increases when the film thickness decreases. In particular, a decrease in the relative quantum yield for BP films of $0.5\text{-}1$ and $0.05\text{-}0.01 \mu\text{m}$ in thickness is ~ 5 at $T = 60 \text{ K}$ and 50% as compared to that at $T = 4.2 \text{ K}$, correspondingly. When the temperature reaches $80\text{-}90 \text{ K}$, these values change to ~ 50 and more than 90% , respectively. Such

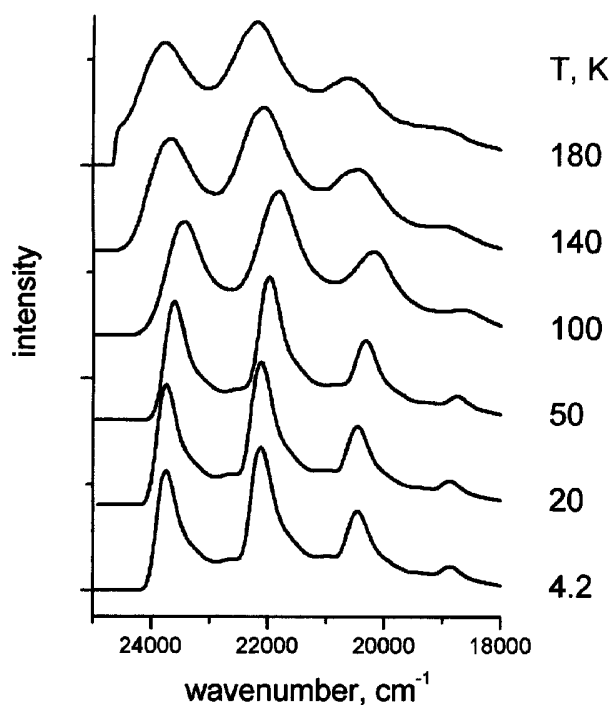


Fig. 3. Phosphorescence spectra of the BP amorphous (glass-like) phase presented for some selected temperatures of the studied region ($4.2\text{-}180 \text{ K}$)

a temperature dependence of the phosphorescence intensity of the thin films can be explained as follows. When the thickness of a BP layer decreases and reaches the value comparable to the diffusion shift length of triplet excitations at a given temperature, the film surface starts to efficiently quench triplet excitons. This process is accompanied with a decrease in the phosphorescence life-time and quantum yield. Thus, a significant decrease in the intensity of the series I phosphorescence bands observed at $T > 70\text{-}80 \text{ K}$ suggests that these bands originate from the luminescence of amorphous BP films, which are formed on the surface of TiO_2 nanoparticles and have a thickness not more than $0.05\text{-}0.1 \mu\text{m}$. This conclusion is in a qualitative agreement with the results obtained during the investigations of similar heterogeneous systems by IR and Raman spectroscopies [23].

Concerning the bands of series II observed in the phosphorescence spectra of the TD-BP heterogeneous system, we assign them to the presence of the BP crystalline phase in the sample. The small value of the red shift ($\sim 100 \text{ cm}^{-1}$) observed for this series when the sample is heated from 10 to 180 K and the peak position of the main band at $T = 4.2 \text{ K}$ are close to those observed for the polycrystalline BP samples in the temperature range of $4.2\text{-}180 \text{ K}$ [24]. It is interesting to note that a similar co-existence of two

structural modifications was observed in our previous paper [25] for BP capsulated into the channels of mesoporous aluminosilicate molecular sieves of MCM-41 type. But contrary to the results of the present work, there were two different amorphous phases of BP in the latter case.

Conclusions

In summary, the analysis of the experimental results obtained demonstrates that two types of BP molecules self-organization, namely amorphous and crystalline structures, are realized in the TD-BP heterogeneous system in the temperature range of 4.2–180 K. The amorphous glass-like phase of BP is created in thin (less than 0.05–0.1 μm) near-surface layers, which is a result of BP structure disordering and destroying the long-range alignment in this substance due to the influence of numerous defects of different nature and active centers located on the Fe-modified TiO_2 surface.

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