

Mechanochemical synthesis of barium titanate and its photocatalytic properties*

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The nano-dispersed barium titanate was synthesised by mechanochemical treatment of barium titanate oxalate and mixture of BaO and TiO₂. Prepared barium titanate demonstrates higher photoactivity in comparison to the same sample obtained by traditional solid state reaction. Shift of absorption edge in the visible region and respective narrowing of the band gap for the milled samples were observed.

1. INTRODUCTION

Protection of the environment and application of “green chemistry” methods to industrial technologies are the most relevant problems of modern fundamental and applied science [1,2]. In particular, photocatalytic reactions such as decomposition of pollutants in water and air receive great attention [3]. It is known that some metal titanates have interesting photocatalytic properties. Thus photoactivity of strontium titanate in various processes of wastes neutralization was shown in works [4-6]. The photocatalytic properties of barium titanate (BT) used as traditional electroceramic material (for example, ferroelectric) and their relationships with dielectric parameters were described in papers [7-11]. In this work we present the properties of BT prepared from different raw materials by mechanochemical synthesis which permits to obtain BT powders with high specific surface area in mild conditions. It is known that the mechanochemical

*This article is dedicated to Professor Roman Leboda on the occasion of his 65th birthday

synthesis (MChT) relates to non-conventional methods of green chemistry since it allows to decrease the pollution in the environment [12-15]. It is necessary to note that influence of MChT on photoactivity of BT was not studied while the MChT modification of titanium dioxide was reported in some papers [16-20].

2. MATERIALS AND METHODS

The mechanochemical synthesis of barium titanate was carried out in a planetary ball mill Pulverisette 6 (Fritsch GmbH) in air atmosphere. Ten silicon nitride balls with a diameter of 15 mm (total mass was 130 g) and the vessel of silicon nitride (250 ml) were used. The amount of milled reagent or mixture of reagents was equal to 10 g. Time of treatment was varied from 2 up to 10 h.

Two pathways of BT preparation were used: **(I)** MChT of barium titanate oxalate (BTO) production of "Ferro" and **(II)** MChT of the mixture of barium and titanium oxides. In the latter case different compounds of titanium oxide with the specific surface area $S = 4\text{--}360 \text{ m}^2/\text{g}$ were used: anatase, rutile, brookite, and their mixtures, metatitanic acid, amorphous oxide (Table 1). After MChT all samples were calcined (TT) in air at $300\text{--}800^\circ\text{C}$ for 2 h.

The phase composition (XRD) of the obtained samples was determined with a diffractometer PW 1830 (Philips) using CuK_α radiation. Thermogravimetric analysis was performed using Derivatograph-C (MOM, Budapest) in air with the heating rate $- 10^\circ/\text{min}$ in the temperature range $20\text{--}800^\circ\text{C}$ (sample weight $- 50 \text{ mg}$). The FTIR spectra in the range $2500\text{--}400 \text{ cm}^{-1}$ were registered using a Perkin-Elmer spectrometer "Spectrum - One" (pellets with KBr at the mass ratio 1:20). The electron spectra of the samples were obtained using a spectrometer UV-VIS SPECORD M 40 (standard - MgO). The specific surface area was calculated by means of the BET method from the adsorption-desorption isotherms of nitrogen ("NOVA-1200", Quantochrome Instruments).

For determination of the prepared samples photocatalytic properties, the degradation of safranin T in aqueous solution under UV-irradiation ($\lambda_{\text{max}} = 254 \text{ nm}$, 30 W) was used as a test reaction. This textile dye, on one hand, is a harmful pollutant for the environment and, on the other hand, it is very stable to influence visible light and therefore suitable for photocatalytic investigations. The optimal conditions for the safranin T photodegradation were found in accordance with the data [21]: dye concentration $- 0.5 \cdot 10^{-5} \text{ mol/l}$, catalyst/solution ratio = 92 mg/46 ml, vigorous stirring of dispersion. In determined times about 5 ml aliquot of the dye solution was withdrawn and after separation on the centrifuge, it was analyzed a spectrophotometer (Lambda 35, Perkin-Elmer Instruments) at $\lambda_{\text{max}}=520 \text{ nm}$.

3. RESULTS AND DISCUSSION

3.1 Preparation of barium titanate (BT) from barium titanyl oxalate (BTO) – pathway I

The data presented in Figure 1 show the XRD patterns of initial BTO and the products of its transformation during traditional thermal treatment (TTT) according to [22] and MChT with and without subsequent thermal treatment TT (figures in brackets show the temperature of TT in °C).

Tab. 1. The properties of some BT powders prepared by MChT (time of treatment 5 h)*

NN	Treatment	S _{TiO} , m ² /g	PhCaT	I ₁₀₁ /I ₀₀₂	D ₁₀₁ , nm	S _{BaTiO₃} , m ² /g	D _s , nm	K _d ·10 ⁵ , s ⁻¹
1	TTT (700)	0.1	BTO + BT	100/31	15.7	6.8	147	n.d.
2	TTT (800)		BT	100/26	16.8	5.3	208	2.3
3	Pathway I, MChT		BT	0/100	-	23.1	43	4.3
4	Pathway I, MChT +TT (550)		BT	100/29	15.0	19.6	51	3.4
5	Pathway I, MChT +TT (700)		BT	100/31	16.5	17.5	57	3.1
6	Pathway I, MChT +TT (800)		BT	100/36	18.5	14.2	70	2.8
7	Pathway II, TiO ₂ =B+A, MChT	54	BT	100/28	18.0	48.0	21	8.1
8	Pathway II, TiO ₂ =B+A, MChT**		BT	100/32	13.2	49.0	20	7.8
9	Pathway II, TiO ₂ =A+R, MChT	65	BT+R	100/40	7.8	79.0	13	4.0
10	Pathway II, TiO ₂ =amorph, MChT	380	BT	100/37	12.0	65.0	15	4.6
11	Pathway II, TiO ₂ =A, MChT	103	BT	100/36	15.1	45.0	22	6.4

* S_{TiO} – specific surface area of initial Ti-containing reagents, PhCaT – phase composition of the samples after treatment, D₁₀₁ – crystallite size calculated from the XRD data, S_{BaTiO₃} – specific surface area of treatment products, D_s – effective particle size calculated from S_{BaTiO₃}, K_d – rate constant of safranin T degradation, TiO₂=B, A, R – brookite, anatase and rutile, correspondingly

**treatment time was 10 h

It was established that after two hours of MChT of BTO the complete destruction of initial compound crystalline structure takes place. Simultaneously the appearance of some reflexes of cubic BaTiO₃ was observed. The increase of treatment time up to 5–10 hours insignificantly changes the intensity of all reflexes on diffractograms (Figure 1, curve 2). The complete absence of the reflex corresponding to (101) plane of cubic BT (d = 0.284 nm) and some other reflexes of this compound can be due to a defective structure of formed BT. Post-annealing of this BT at 550⁰C contributes to improvement of its structure and appearance of all reflexes characteristic of BaTiO₃ (Figure 1, curve 3) with intensities corresponding to those reported in literature. The XRD patterns of this sample demonstrate some difference with the same BT prepared by TTT of BTO at 800⁰C (Figure 1, curve 4).

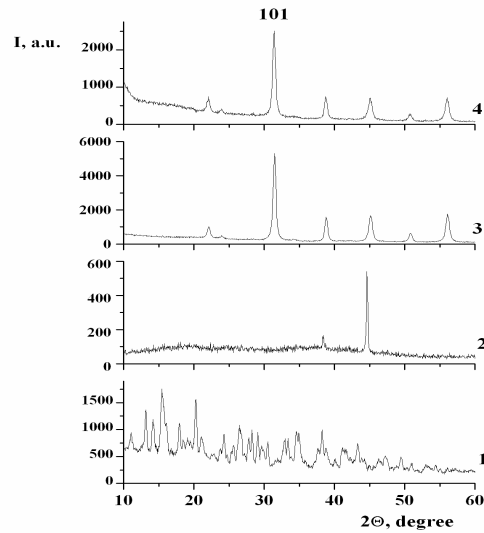


Fig. 1. XRD patterns of initial BTO – 1, and BTO after MChT – 2, MChT + TT (550) – 3, and TTT (800) – 4.

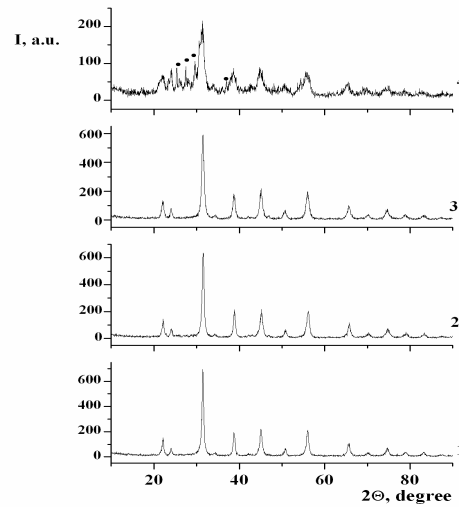


Fig. 2. XRD patterns of BT prepared by pathway **II**: $\text{TiO}_2=\text{B}+\text{A}$ – 1, $\text{TiO}_2=\text{A}$ – 2, $\text{TiO}_2=\text{amorph.}$ – 3, $\text{TiO}_2=\text{A}+\text{R}$ – 4. The reflexes of initial oxides marked by ●.

But the data presented in Table 1 show that the sample prepared by MChT has higher values of specific surface area and simultaneously smaller size of particles and crystallites than the same obtained as a result of TTT (No 2, Table 1). The increase of TT temperature decreases the specific surface area and

particles dimensions of the sample obtained by pathway I (Table 1, No 4, 5, 6) but their values remain much larger and smaller, correspondingly, than for the sample prepared by the traditional technique. So, the use of MChT permits to obtain the nanodimension particles of BaTiO₃ in contrast to known thermal decomposition of BTO.

3.2 Mechanochemical synthesis of barium titanate (BT) from metal oxides – pathway II

MChT of mixtures of BaO with various modifications of TiO₂ led to formation of BT in all cases, but if the brookite, rutile or rutile-anatase mixtures were used as the initial TiO₂-containing compounds, the presence of these oxides in the treated samples was observed also (see, for example, Figure 2, curve 4, and Table 1). The use of anatase, amorphous TiO₂, or anatase-brookite mixture leads to formation of BT only (Figure 2, Curves 1-3, and Table 1).

The results presented in Table 1 show that the BT samples prepared by chemical interaction of BaO and TiO₂ have much larger value of specific surface area and smaller dimension of crystallites than BT obtained in pathway I. The increase of treatment time decreases the size of crystallites and leads to some growth of BT specific surface area. Some correlation between the values of specific surface area of formed BT and initial TiO₂ is found. The comparison of D₁₀₁ and D_s indicates the weak aggregation of crystallites in the case of pathway II.

3.3 Photodegradation of safranin T on BT prepared by MChT

The example of safranin T aqueous solutions of absorbance spectra change in the time of its UV-irradiation in the presence of BT powder prepared by MChT is given in Figure 3. It was found that in all cases the obtained results of dye decolorizing i.e. photodegradation can be described by the first-order kinetic equation (see, for example, Figure 4), which was found by other researchers earlier [11,21,23].

The values of photodegradation constant rate K_d calculated from the plots of ln D – time (where optical density D = f (dye concentration)) for the studied samples are presented in Table 1.

It can be seen that K_d is maximal for the milled sample. The latter fact can be explained in the following way. It is well known that milling results in appearance of structural defects in solids [12] which play a part of additional catalytically active centres [24] included in photocatalytic processes [6,11,19,25]. Milling leads to titanium reduction and formation of oxygen vacancies at grain boundaries. In other words, MChT of BaO and TiO₂ mixture may promote appearance of on pair Ti³⁺ – oxygen vacancy that on the surface is confirmed experimentally for titanium dioxide in [6,19]. Oxygen can be adsorbed on such

surface defects and form superoxide ions O_2^- by interaction with electron [26]. This highly active ion can stimulate destruction of substrate (dye).

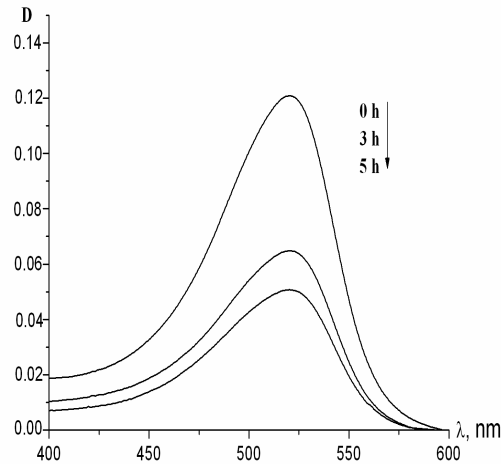


Fig. 3. The absorption spectra of safranin T aqueous solution after different times of UV-irradiation in the presence of BT prepared powder.

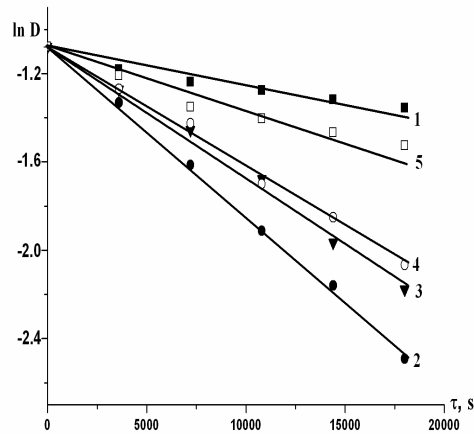


Fig. 4. The kinetic curves of safranin T degradation in the BT samples prepared from the mixture B + A: 1 – usual SSI – 1, MChT: as received – 2, after TT at 400, 600 and 800°C – 3, 4, 5, correspondingly.

As mentioned above S decreases steadily at temperature elevation of post-annealing. On the other hand, photocatalytic activity, namely K_d , changes non-monotonically. Thus, its value decreases for the sample calcined at 300°C that is

caused by lowering of specific surface area and “healing” (relaxation) of defects. Besides, the value of K_d has a local maximum at 400–600°C in spite of further decreasing of specific surface area. This phenomenon, in our point of view, can be associated with appearance of new active centers namely structure defects (probably the same nature as after milling) in this temperature interval due to removal of surface OH-groups. DTA-TG data indicate mass loss equal 1.3–1.8 % w/w (Figure 5) that agrees with literature data [27]. At temperature higher than 600°C the values S and K_d diminish consistently.

It is remarkable that all BT samples, prepared via milling of oxide mixtures, regardless of nature initial TiO_2 are more active than BT produced by solid state interaction of oxides at 1100°C. It should be noted that BT, synthesized through usual thermodestruction of BTO (sample 6 in Table 1), also possesses smaller photoactivity ($K_d=2.3 \text{ c}^{-1}$) comparatively that for the milled samples obtained from BTO ($K_d=4.3 \text{ c}^{-1}$). However, in contrast to the milled samples (route II), for BT, prepared via MChT of BTO (route I), at higher temperature of next calcinations both the specific surface area and the constant of photodegradation rate K_d decrease monotonically and synchronously and crystallite size, vice versa, increases (Table. 1, samples 1-4). Absence of local maximum for K_d at 400–600°C can be explained by overlapping of processes of formation of BT phase through BTO decomposition and removal of OH-groups in this temperature interval.

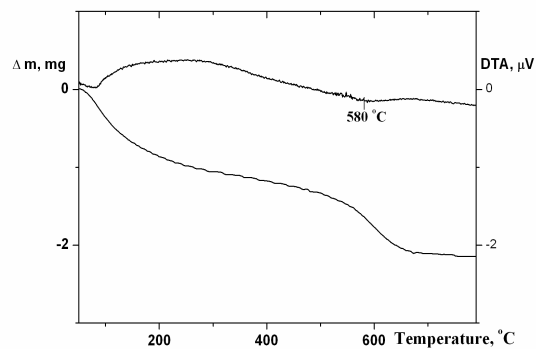


Fig. 5. The curves DTA-TG of BT sample prepared via MChS from anatase+brookite.

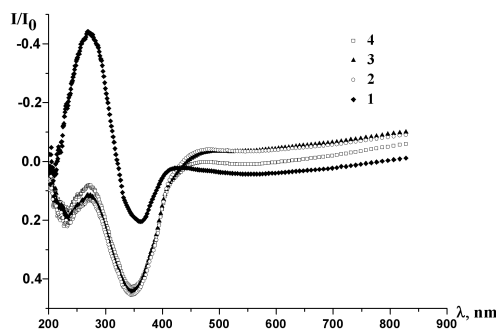


Fig. 6. The UV-VIS spectra of BT samples: BT “Ferro” – 1, prepared by MChT of mixture B + A: as received – 2, after TT (600) – 3 and TT (400) – 4.

3.4. UV-VIS study of milled BT

Another interesting effect significant for singular photochemical properties of milled BT, produced by both routes, was revealed by means of UV-VIS spectroscopy which characterizes the electronic structure of the surface. The UV-VIS spectra for the obtained BT samples are presented in Figure 6. One can see an insignificant increase of absorption in the visible range (for wavelengths larger than 400 nm) for milled BT as well as for the samples post-calcined at 400–600°C. It is known that the absorption edge of semiconductors may vary with crystal size, lattice strain or disordering and amorphization [18]. All listed effects take place during mechanochemical treatment. This causes the formation of additional electronic states in the band gap on the BT surface. The authors [6,19,28] observed a similar effect for mechanochemically activated and doped titanium dioxide and strontium titanate.

Another attractive peculiarity of milled BT, which can be seen from the UV-VIS spectra, is shift of the absorption edge λ in the visible region for these samples in comparison with BT prepared via common solid state reaction (thermdestruction of BTO or interaction of oxides). It should be noted that till now the analogous result was stated solely in consequence of doping of semiconductors by metals or metalloids [6,20,28]. The value observed displacement achieves 53 nm: from 407 nm for the common “solid state” sample to 445–460 nm for various milled BT (Table 2). This effect like increasing photoactivity can be associated with the presence of defects in the samples milled and calcined under 400–600°C. After annealing of milled BT at 300°C and 800°C, when partial relaxation of defects occurs, shift of absorption edge is essentially smaller.

As a result of indicated change in absorption spectra narrowing of the band gap E_g for the milled samples, calculated in accordance with equation [28]:

$$E_g = 1239.8/\lambda$$

from 3.05 for BT prepared by means of usual solid state reaction to 2.70–2.80 eV for those obtained by milling and next calcinations at 400–600°C take place. The latter can be also explained by appearance of structural defects in BT. Shift of absorption edge and narrowing of band gap toward the initial value for the sample, annealed at 700–800°C (Table 2), when relaxation of defects occur, is the evidence for the assumption. On the other hand, this means that milled BT can also possess some photocatalytic activity in the visible region e.g. at irradiation with the wavelength > 400 nm. Observed phenomena extend possibilities of application of such samples.

It should be noted that permittivity ε which is the higher, the more perfect is crystal structure of BT, changes oppositely at elevation of annealing temperature (last line of Table 2).

Tab. 2. Some properties of the sample prepared by mechanochemical synthesis from BaO with TiO₂ (Anatase with Brookite) and calcined at different temperatures.

t, °C	As received	300	400	500	600	700	800
S, m ² /g	48	42	38	35	31	26	21
K _d ·10 ⁵ , c ⁻¹	8.1	5.0	6.1	7.1	6.5	4.7	2.5
E _g , eV	2.70	2.87	2.79	-	2.75	2.80	2.93
E	11	18	20	16	12	21	29

Recently barium titanate based waste materials, are produced on a large scale in industrial fabrication of ceramic capacitors and related devices [29]. There is, however, no effective utilization of used barium titanate with an environmentally acceptable process. In our opinion, mechanochemical activation of such BT with the purpose of effective photocatalysts preparation can be one of the variants for recycling of wastes.

4. CONCLUSIONS

It was established that mechanochemical treatment permits to prepare the nano-dimension barium titanate with lesser particle sizes and larger specific surface area than the traditional methods. The photocatalytic activity of the prepared samples in dye neutralization exceeds that characteristic of traditionally prepared compositions.

The obtained results show that the BT samples prepared by MChT can possess some photocatalytic activity in the visible region e.g. at irradiation with

the wavelength > 400 nm. This fact extends the possibilities of application of barium titanate produced on a large scale in manufacture of ceramic capacitors and related devices in the reactions of environment protection.

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5. REFERENCES

- [1] P. Cintas, J. L. Luche, *Green Chemistry*, 1, 115 (1999).
- [2] P. T. Anastas, M. M. Kirchoff, T. C. Williamson, *Appl. Catal. A*, 221, 3 (2001).
- [3] A. Linsebigler, G. Lu, J. T. Yates, *Chem. Rev.*, 95, 735 (1995).
- [4] J. G. Mavrodiss, J. A. Kafalas, 1976, *Appl. Phys. Lett.*, 28, 241 (1976).
- [5] S. Ahuja, N. T. Kutty, *J. Photochem. Photobiol. A.*, 97, 99 (1996).
- [6] J. Wang, S. Yin, M. Komatsu, Q. Zhang, F. Saito, T. Sato, *Appl. Catal. B*, 52, 11 (2004).
- [7] B. Zielińska, E. Borowiak-Palena, R. J. Kalenczuka, *Int. J. Hydrogen Energy*, 33, 1797 (2008).
- [8] V. V. Sydoruchuk, V. A. Zazhigalov, S. V. Khalameida, K. Wieczorek-Ciurowa, J. Skubiszewska-Zięba, R. Lebeda, *J. Alloys and Compd.*, in press, (2009).
- [9] J. L. Giocordi, G. S. Rohrer, *Chem. Mater.*, 13, 241 (2001).
- [10] Q. S. Li, K. Domen, S. Naito, *Chem. Lett.*, 3, 321 (1983).
- [11] D. Demydov, *Nanosized alkaline earth metal titanates: effects of size on photocatalytic and dielectric properties*, Thesis Kansas State University, Manhattan, 2006, p. 226.
- [12] E. Avvakumov, M. Senna, N. Kosova, *Soft Mechanochemical Synthesis*, Kluwer Acad. Publ., Boston, 2002, p. 210.
- [13] K. Wieczorek-Ciurowa, K. Gamrat, *J. Therm. Anal. Calorim.*, 88, 213 (2007).
- [14] Y. Tanaka, Q. Zhang, F. Saito, *J. Mater. Sci.*, 39, 5497 (2004).
- [15] N. Stevulova, T. Sverak, *Chem. Listy*, 99, 649 (2005).
- [16] M. C. Hidalgo, G. Golon, J. A. Navio, *J. Photochem. Photobiol. A*, 148, 1 (2002).
- [17] M. Uzunova-Bujnova, D. Dimitrov, D. Radev, A. Bojinova, D. Todorovsky, *Mater. Chem. Phys.*, 110, 291 (2008).
- [18] U. Gesenhues, *J. Phys. Chem. Solids*, 68, 224 (2007).
- [19] S. Indris, R. Amade, P. Heitjans, M. Finger, A. Haeger, D. Hesse, W. Grünert, A. Börger, K. D. Becker, *J. Phys. Chem. B*, 109, 23274 (2005).
- [20] S. Yin, Q. Zhang, F. Saito, T. Sato, *Chem. Lett.*, 32, 358 (2003).
- [21] V. K. Gupta, R. Jain, A. Mittal, M. Mathur, S. Sikarwar, *J. Colloid Interface Sci.*, 309, 464 (2007).
- [22] Y. S. Kholam, A. S. Deshpande, H. S. Potdar, *Mater. Lett.*, 55, 175 (2002).
- [23] C. Guillard, J. Disdier, J. M. Herrman, C. Lehaut, T. Chopin, S. Malato, J. Blanco, *Catal. Today*, 54, 217 (1999).
- [24] I. Ayub, D. Su, M. Willinger, A. Kharlamov, L. Ushkalov, V. Zazhigalov, N. Kirillova, R. Schlögl, *Phys. Chem. Chem. Phys.*, 5, 970 (2003).
- [25] H. Liu, H. T. Ma, Z. W. Li, M. Wu, X. H. Bao, *Chemosphere*, 50, 39 (2003).
- [26] R. F. Howe, M. Grätzel, *J. Phys. Chem.*, 91, 3906 (1987).
- [27] P. Badheka, L. Qi, B. Lee, *J. Eur. Ceram. Soc.*, 26, 1393 (2006).
- [28] G. Liu, F. Li, Z. Chen, G. Q. Lu, H. -M. Cheng, *J. Solid State Chem.*, 179, 331 (2006).
- [29] K. Kikuta; Y. Shimizu, M. Moriya, T. Yamaguchi, S-I. Hirano, Y. Saito, T. Miyoshi, H. Yamamoto, Y. Sakabe, *J. Ceram. Soc. Japan*, 114, 392 (2006).