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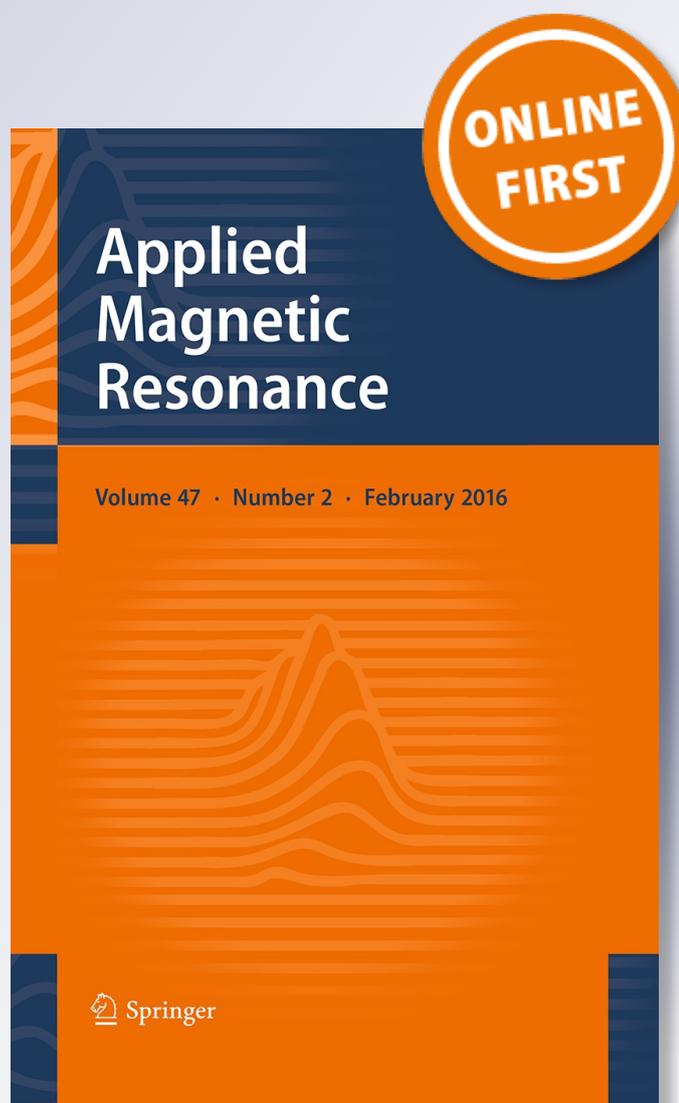
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EPR Study of TiO$_2$ (Rutile) Doped with Vanadium

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Abstract Samples of titanium dioxide, TiO$_2$, doped with vanadium ions $(0.1 \leq [V^{n+}]_0 \leq 5.0$ at. %) at high temperature, were prepared in a polycrystalline state and investigated using X-, Q-, and W-band electron paramagnetic resonance, EPR, spectroscopy. Substitutional and interstitial V^{4+} centers in TiO$_2$ lattice have been both observed in EPR spectra, and their spin-Hamiltonian parameters were calculated. Portions of paramagnetic and diamagnetic species of V^{n+} ions were estimated. The effect of additional high temperature annealing on the valence state of vanadium centers is discussed.

1 Introduction

During last 35–40 years, a numerous amount of papers have been published concerning titanium dioxide materials modified with different metal and non-metal atoms. TiO$_2$-based compounds are widely used as effective photocatalysts for decomposition of highly toxic organics including chloro organic compounds [1–12], as electrodes for photoelectrochemical conversion of solar energy [13–16] as well as titanium-vanadium catalysts in many industrial processes [17–19]. In all cases,

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titanium dioxide has been used in the form of anatase, rutile or their mixtures. Since TiO_2 is ecologically safe, being a wide-gap semiconductor, it seems to be a promising starting material for the development of new effective photocatalysts.

The main disadvantage of TiO_2 as a photoactive support is its large gap of the forbidden band ($E_g = 3.1$ eV for rutile and ≈ 3.0 eV for anatase) of the semiconductor, i.e., only light of the nearest UV region of the solar spectrum can be absorbed at the wavelengths $\lambda < 400$ nm. One of the possible ways for enhancement of the photosensitivity of TiO_2 and the improvement of its photochemical properties at $\lambda > 400$ nm is its doping or modification with the transition metal ions [20, 21]. The doping of single crystalline (SC) and polyc1ystalline (PC) TiO_2 in the rutile form noticeable changes the electrophysical and photoelectrochemical properties of titania [20–23]. The spectral sensitivity of TiO_2 materials can be reasonably extended to the long-wave region by doping with V^{4+} or Cr^{3+} ions [23–25].

In this paper, the spectroscopic features of the polycrystalline, PC, TiO_2 (rutile) doped with vanadium ions, obtained using X-, Q- and W-band electron paramagnetic resonance, EPR, spectroscopy are reported. The role of high temperature annealing as a factor affecting properties of V–TiO_2 system are discussed.

2 Experimental

Powders of pure TiO_2 and of V_2O_5 were stirred thoroughly at the required ratios and the briquettes were compressed of these mixtures under pressure of 250 kg s/cm². Then, the briquettes were thermally treated. Firstly, temperature was slowly increased till 600 °C at 2°/min, and at this temperature the samples were treated during 10 h. Then, the briquettes were grinded again in an agate mortar and pressed again into briquettes, which were thermally treated for 2 h at 1200 °C in an inert medium (He). Afterwards, temperature decreased at 50°/h. This set of samples with total vanadium content of $0.1 \leq [V^{n+}]_0 \leq 5.0$ at. % has been investigated using EPR technique. In these samples, the matrix contained an uncontrolled amount of oxygen vacancies. For removing them, some samples were additionally annealed in air for 2 h at 900 °C. After the last procedure, the samples became dark colored both on the surface and in the bulk. Homogeneity of the resulting samples was tested by the X-ray diffraction analysis, which showed that all doped samples up to vanadium content of 5 at. % retained uniformity and had the structure of the initial rutile [25].

EPR measurements of the polycrystalline samples were performed on an X-band Bruker EMX-8 spectrometer at 77 K. The spectrometer frequency was 9.65 GHz, a modulation frequency of 100 kHz and a microwave power of 0.5 mW were used. Also, the EPR measurements were carried out on a Bruker ELEXSYS E 580 spectrometer at Q-band and on an ELEXSYS E 680 spectrometer with superconducting magnet at W-band in the temperature range of 80–40 K. The sample temperature was controlled in a helium gas-flow cryostat (Oxford). The spin-Hamiltonian parameters: the hyperfine splitting, hfs, constants on vanadium ^{51}V atom. A_x, A_y, A_z, and g-values g_x, g_y, g_z for the X-,Q- and W-band spectra were

calculated by the computer simulation of the experimental EPR spectra. EPR spectra fits were done using the computer program package developed by Prof. A. Kh. Vorob'ev (Department of Chemistry, M. V. Lomonosov Moscow State University).

The absolute amounts of paramagnetic vanadium ions [V^{4+}] in the samples, in spin/g, were evaluated by double integration of the spectra and by comparison of the results with a reference: the spectrum of a CuCl$_2$·2H$_2$O single crystal with known number of spins. The Mn^{2+} admixture in MgO was used for a precise graduation of EPR spectra.

3 Results and Discussion

Typical X-band EPR spectra at 77 K of TiO$_2$ doped with 0.1 at. % of vanadium just after synthesis of the polycrystalline V-TiO$_2$ material and after additional high-temperature annealing at 900 °C in air are shown in Fig. 1. Computer analysis of the spectra reveals that experimental spectrum (*a*) is a superposition of two different paramagnetic centers. Subtracting spectrum (*b*) from spectrum (*a*), we obtained spectrum (*c*) which is enlarged five-fold in Fig. 1. The spin-Hamiltonian parameters calculated from EPR spectra modeling (*b'*, *c'*) are listed in Table 1. It should be noted that computer fitting of the X-band spectra gives $\langle g \rangle$ and $\langle A \rangle$ values with a relatively high precision.

Increasing of the vanadium content to [V^{n+}]$_0$ = 0.3 at. % and higher results in existing of only one type (*b*) of paramagnetic centers without any traces of the spectrum (*b*) even without additional high temperature annealing. EPR spectra analysis allowed us to conclude that maximum content of the interstitial centers

Fig. 1 X-band EPR spectra at 77 K normalized to the equal weight of V-TiO$_2$ samples at 0.1 at. % of vanadium before (*a*) and after (*b*) annealing at 900 °C in air. The spectrum (*c*) is obtained by subtracting (*b*) from (*a*), the amplitude of (*c*) is enlarged five-fold. Spectra (*b'*) and (*c'*) are computer fits of spectra (*b*) and (*c*) respectively
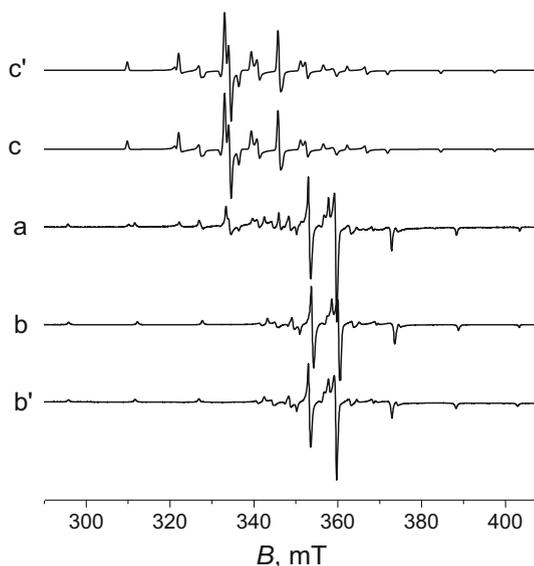
Table 1 EPR parameters (hfs constants are in $10^{-4} \times A_m$, cm^{-1}) of V^{4+} paramagnetic centers in vanadium-doped TiO_2 (rutile) lattices

Sample	g_x^a	g_y	g_z	A_x^a	A_y^a	A_z^b	References
X-band, lat.	1.9160	1.9137	1.9579	30.2	42.6	140.0	This work
X-band, int.[d]	1.9863	1.9914	1.9411	44.3	58.9	110.2	
X-band, int.[e]	1.9826	1.9895	1.9355	45.1	60.1	113.1	
Q-band, lat.	1.9152	1.9132	1.9564	31.0	43.3	143.4	
Q-band, int.	1.9850	1.9902	1.9372	47.1	60.6	102.9	
W-band, lat.[f]	1.9149	1.9128	1.9557	30.2	42.9	141.8	
W-band, lat.	1.9150	1.9130	1.9555	30.3	43.0	142.3	
W-band, int.	1.9836	1.9890	1.9363	46.6	60.7	102.9	
V-TiO$_2$, lat.	1.915	1.913	1.958	31.8	45.5	151.3	[26]
V-TiO$_2$, int.	1.986	1.9935	1.9405	48.5	64.5	121.5	
PC	1.913	1.913	1.956	31	45	156	[27]
PC	1.914	1.912	1.956	31	44	142	[28]
SC	1.915	1.913	1.956	31	43	142	[29]
SC	1.913	1.912	1.955	31	44	141.5	[30]
SC, int.	1.9865	1.9930	1.9407	45.4	60.5	111.4	[31]
Theory	1.917	1.893	1.966	35	40	141	[32]
NC[c]	1.906	1.899	1.941	27.6	45.2	138	[33]

[a] The accuracy of measurements in X-band is: $g_m \pm 0.003$, $A_n \pm 2 \times 10^{-4}$ cm^{-1}

[b] $A_z \pm 3 \times 10^{-4}$ cm^{-1}

[c] NC, lat., int. mean nanocrystalline particles, lattice, intersticial correspondingly

[d] From the whole spectrum fit

[e] From the subtracted spectrum

[f] From single spectrum

does not exceed $(3–4) \times 10^{17}$ spin/g, what is approximately tenfold less comparing to the amount of substitutional V^{4+} species in the same sample.

Figure 2 presents EPR spectra of the same samples recorded at the Q-band, because of the higher external magnetic field, the resolution of lines reflecting Zeeman interaction at *x*- and *y*- orientations became more evident. In this case, EPR parameters obtained from the computer fitting of the Q-band experimental spectra (*a′*. *b′* in Fig. 2) are calculated with higher precision. They are also given in the Table.

The best resolution of the intersticial and substitutional EPR spectra in the same samples has been achieved with recording at the W-band which are shown in Fig. 3. Parameters of the computer fitting are also listed in the Table.

It follows from the results given in the Table as well as in publishes in Ref. [34] that (a) the nature of the V^{4+} ion location in the TiO_2 lattice: substitutional or intersticial, influences noticeably on $\langle g \rangle$ and $\langle A \rangle$ values, which are principly different: $g_x, g_y > g_z$ for interstitial, $g_x, g_y < g_z$ for the substitutional ions, while in both cases $A_x, A_y < A_z$; (b) values measured fon single crystals and polycrystalline
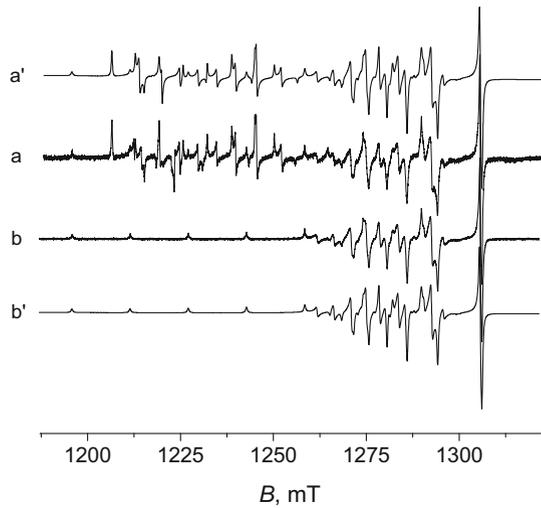
Fig. 2 Q-band EPR spectra at 40 K normalized by amplitude of V-TiO$_2$ samples at 0.1 at. % of vanadium before (*a*) and after (*b*) annealing at 900 °C in air. Spectra (*a'*) and (*b'*) are the computer fits of spectra (*a*) and (*b*) respectively
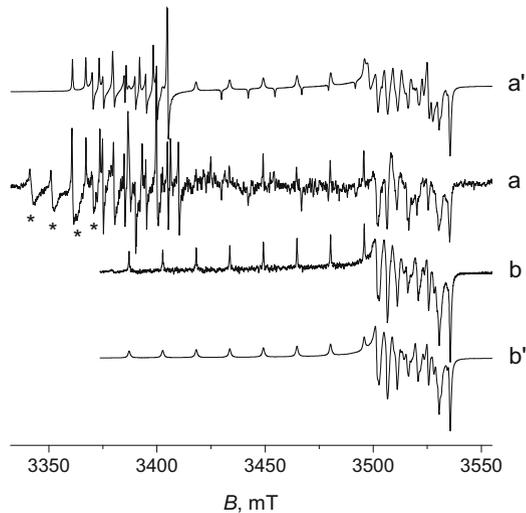
Fig. 3 W-band EPR spectra at 40 K normalized by amplitude of V-TiO$_2$ samples at 0.1 at. % of vanadium before (*a*) and after (*b*) annealing at 900 °C in air. Spectra (*a'*) and (*b'*) are the computer fits of spectra (*a*) and (*b*) respectively. Asterisks denote four first lines of a Mn^{2+} admixture in MgO spectrum

materials are practically coinside; (c) structural peculiarities of NC particles, reflecting in EPR parameters, are noticeably different from those of SC and PC cases; (d) at the first time in polycrystalline titania, both types of doping paramagnetic vanadium V^{4+} centers were observed at once in the same sample.

Double integration of EPR spectra of V-Tio$_2$ samples containing different amount of the doping vanadium (Fig. 4) shows that the content of paramagnetic V^{4+} ions in the TiO$_2$ lattice, [V^{4+}], increasing slightly at the beginning up to [V^{n+}]$_0 \leq 0.5$ at. %, monotonously decreases afterwards. Comparing the measured [V^{4+}] values in the titania matrix with the whole titanium content at [V^{n+}]$_0 > 1.0$
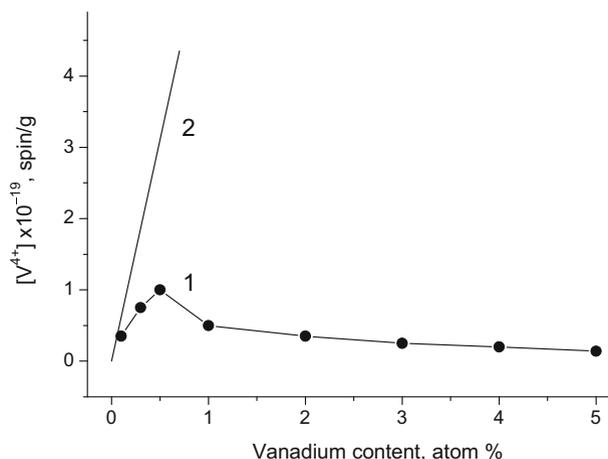
Fig. 4 Concentration of paramagnetic vanadium ions $[V^{4+}]$ as a function of the total vanadium content $[V^{n+}]_0$. *Line 2* shows the corresponding increase of $[V^{n+}]_0$

at. %, i.e., $>6.1 \times 10^{19}$ spin/g, one can conclude that the main part of doped vanadium ions are diamagnetic (more than 90 %), being in the valent state of V^{5+}. At $[V^{n+}]_0 = 5.0$ at. %, a portion of paramagnetic V^{4+} ions does not exceed 0.5 % of the total vanadium content $[V^{n+}]_0$.

Comparing our present results with those obtained for the high-temperature annealed V-TiO$_2$ samples reported in [26], we would like to emphasize that such annealing move all previously diamagnetic vanadium species to the paramagnetic state, i.e., from V^{5+} to V^{4+} ions. V-TiO$_2$ centers observed in [26] were of only a substitutional type, and their concentration linearly increased with the increase of $[V^{n+}]_0$. Photophysical and photoelectrochemical properties of the samples described in Ref. [26] were more stable and reproducible in time.

4 Conclusion

Samples of titanium dioxide TiO$_2$ (rutile) doped with vanadium ions $(0.1 \leq [V^{n+}]_0 \leq 5.0$ at. %) prepared under high temperature synthesis in a polycrystalline state were investigated using X-, Q- and W-band EPR spectroscopy. Substitutional and interstitial V^{4+} centers in V-TiO$_2$ lattice have been both observed in EPR spectra at $[V^{n+}]_0 = 0.1$ at. %. Their spin-Hamiltonian parameters were calculated from EPR spectra simulations. Portions of paramagnetic and diamagnetic species of V^{n+} ions were calculated, and the additional high temperature annealing of the samples changed the valence state of vanadium centers from diamagnetic V^{5+} to paramagnetic V^{4+} ions.

References

1. N. Serpone, E. Pelizzetti (eds.), *Photocatalysis: Fundamentals and Applications* (John Wiley & Sons, New York, 1989)
2. M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Chem. Rev. **95**, 69 (1995)
3. D.F. Ollis, H. Al-Ekabi (eds.), *Photocatalytic Purification and Treatment of Water and Air* (Elsevier, Amsterdam, 1993)
4. A. Fujishima, T.N. Rao, D.A. Tryk, J. Photochem. Photobiol. C, Photochem. Rev. **1**, 1–21 (2000)
5. X. Chen, S.S. Mao, Chem. Rev. **107**, 2891 (2007)
6. P.G. Wu, R.A. Xie, K. Lay, J. Kushang, Environ. Sci. Technol. **44**, 6992 (2010)
7. M. Kitano, M. Matsuoka, M. Ueshima, M. Anpo, Appl. Catalysis A, General **325**, 1 (2007)
8. W.-K. Jo, J. Kim, Environ. Eng. Res. **13**(4), 171 (2008)
9. Z. Zheng, B. Huang, X. Qin, X. Zhang, Y. Daib, M.-H. Whangbo, J. Mater. Chem. **21**, 9079 (2011)
10. S.O. Obare, G.J. Meyer, J. Environ, Sci. & Health **A39**, 2549 (2004)
11. T.K. Ghorai, Open. J. Phys. Chem. **1**, 28 (2011)
12. H. Zhang, G. Chen, D.W. Bahnemann, J. Mater. Chem. **19**, 5089 (2009)
13. M. Graetzel (ed.), *Energy Resources through Photochemistry and Catalysis* (Academic Press, New York, 1983)
14. M. Schiavello (ed.), *Photoelectrochemistry. Photocatalysis and Photoreactors* (Reidel Publ. Co., Dordrecht, 1985)
15. E. Pelizzetti, M. Schiavello (eds.), *Photochemical Conversion and Storage of Solar Energy* (Kluwer, Dordrecht, 1991)
16. Yu.V. Pleskov, *Photoelectrochemical Conversion of Solar Energy* (Nauka, Moscow, 1990)
17. I.E. Wachs, R.Y. Saleh, S.S. Chan, C. Chersich, Appl. Catal. **15**, 339 91985)
18. G. Centi, E. Giamello, D. Pinelli, F. Trifiro, J. Catal. **130**, 220 (1991)
19. O.V. Krylov, *Heterogeneous Catalysis*, (IKC "Akademkniga", Moscow, 2004)
20. A.K. Ghosh, H.P. Maruska, J. Electrochem. Soc. **124**, 1516 (1977)
21. T.E. Phillips, K. Moorjani, J.C. Murphy, T.O. Poehler, J. Electrochem. Soc. **129**, 1210 (1982)
22. P. Salvador, Solar Energy Materials **2**, 413 (1980)
23. Y. Matsumoto, J. Kurimoto, T. Shimizu, E. Sato, J. Electrochem. Soc. **128**, 1040 (1981)
24. V.M. Aroutiounian, V.M. Arakelyan, G.E. Shahnazaryan, Sol. Energy Mater. Sol. Cell. **89**, 153 (2005)
25. V.M. Aroutiounian, V.M. Arakelyan, G.E. Shahnazaryan, Sol. Energy **78**, 581 (2005)
26. A.I. Kokorin, V.M. Arakelyan, V.M. Arutyunyan, Russ. Chem. Bull., Inter. Ed. **52**, 93 (2003)
27. A. Davidson, M. Che, J. Phys. Chem. **96**, 9909 (1992)
28. R. Gallay, J.J. van der Klink, J. Moser, Phys. Rev. **34B**, 3060 (1986)
29. H.J. Gerritsen, H.R. Lewis, Phys. Rev. **119**, 1010 (1960)
30. G.M. Zverev, A.M. Prokhorov, Zh Exper, Teor. Fiz. **39**, 222 (1960)
31. F. Kubec, Z. Sroubek, J. Chem. Phys. **57**, 1660 (1972)
32. F.M. Michel-Calendini, G. Fichelle, Phys. Stat. Sol. B **69**, 607 (1975)
33. S.T. Martin, C.L. Morrison, M.R. Hoffmann, J. Phys. Chem. **98**, 13695 (1994)
34. A.I. Kokorin, in: *Chemical Physics of Nanostructured Semiconductors*, eds. A.I. Kokorin, D.W. Bahnemann (VSP–Brill Academic Publishers, Utrecht, Boston, 2003), p. 203