

EPR STUDY OF NANOCRYSTALLINE TiO₂ SUBJECTED TO DIFFERENT MODIFICATIONS

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Abstract. Eight samples of nanocrystalline TiO₂, subjected to three different modifications (various calcination temperatures, N doping levels and water rinsing) have been prepared. The crystallite sizes of all studied samples were determined to be smaller than 15 nm. Electron paramagnetic resonance (EPR) measurements at temperatures 4-290K have been conducted. The EPR spectra displayed a signal, in form of a resonance line, attributed to the trivalent titanium complex. In the low temperature range ($T < 45K$), the temperature dependence of the EPR integrated intensities showed a similar paramagnetic behavior in all cases. At high temperatures ($T > 50K$) a different behavior prevailed and ferromagnetic interactions between the paramagnetic centers were revealed. These interactions are attributed to the presence of free electrons, whose concentration strongly depends on the used modification process.

1. INTRODUCTION

Recently, titanium dioxide and its modifications have been intensively investigated for applications in different materials and devices [1-8]. The presence of electric conductivity in correlated spin systems, at room temperature, promises the use of this material in these electronic systems. It has been suggested that the origin of ferromagnetism in such systems may be connected with exchange interactions between singly ionized oxygen vacancies directly ($F^+ - F^+$), or by mediation of conduction electrons ($F^+ - \text{conduction electrons} - F^+$) [1]. At room temperature, ferromagnetism is observed in Fe-doped TiO₂ [3,6]. An electron, locally trapped by an oxygen vacancy, that occupies an orbital overlapping with the unpaired electron ($3d^1$) of a Ti^{3+} ion and/or the unpaired electron ($3d^5$) of a Fe^{3+} ion, could be

responsible for a ferromagnetic state in titanium dioxide at room temperature [3]. The EPR investigations have revealed two ferromagnetic behaviors: one in the low temperature range 110-160K, with the evaluated Curie temperature being $\theta = 110K$, and one in the high temperature range 170-230K, with $\theta = 165K$ [2].

The purpose of this study was to examine the impact of three different TiO₂ modifications (variation of calcination temperature, N-doping level, and water rinsing) on magnetic properties of nanocrystalline titanium dioxide. EPR measurements were carried out in temperature range 4-290K and the obtained spectra were analyzed, providing information about the properties of the paramagnetic centers and their interactions. Particular attention was paid to the role of trivalent titanium ion and to electron conductivity of the samples.

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Table 1. Samples designation and modification processes they were subjected.

Sample designation	Calcination temperature [$^{\circ}\text{C}$]	N doping level	Water rinsed
1	750	Low	No
2	750	Low	Yes
3	750	High	No
4	750	High	Yes
5	800	Low	No
6	800	Low	Yes
7	800	High	No
8	800	High	Yes

2. EXPERIMENTAL

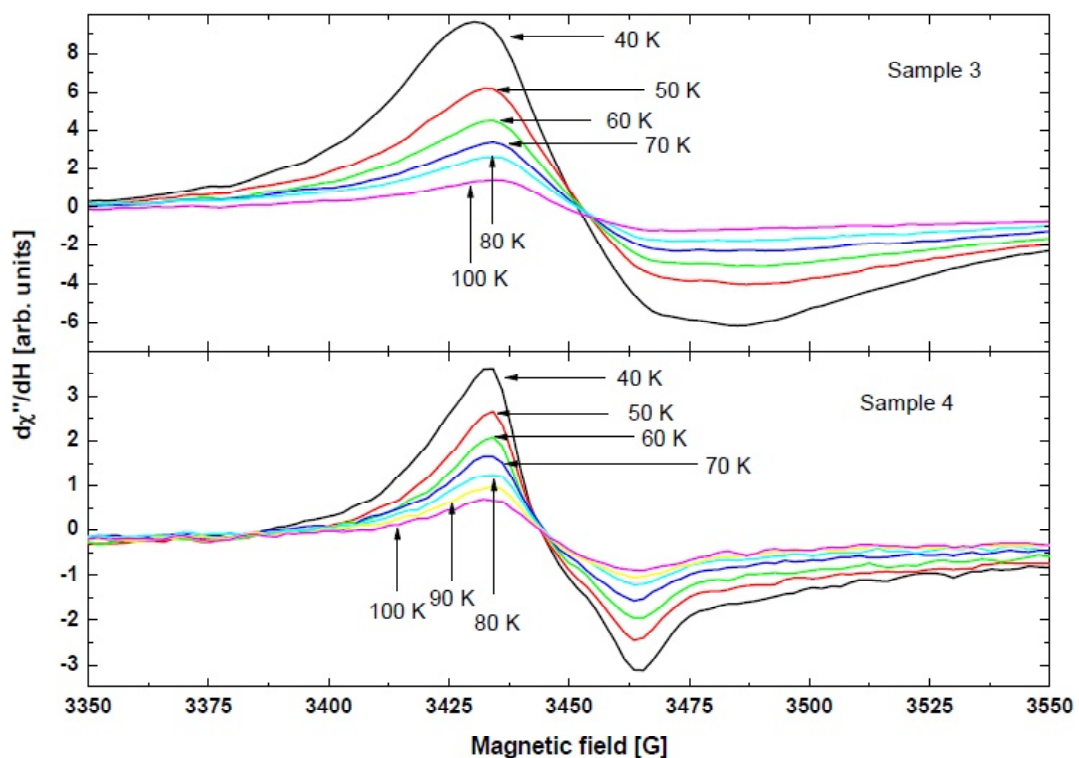
The eight nanocrystalline samples of titanium dioxide and the modification processes they were subjected to, are presented in Table 1. The procedure of nanocrystalline titanium dioxide synthesis has been described in previous works [9,10]. EPR measurements were performed with a conventional X-band ($\nu = 9.4$ GHz) Bruker E 500 spectrometer with 100 kHz magnetic field modulation, equipped with Oxford helium-flow cryostat.

3. RESULTS

Fig. 1 presents the magnetic resonance spectra of samples 3 and 4 at different temperatures, showing

the effect of rinsing with water. The spectra are dominated by a single, intense, broad and strongly asymmetrical line, which is characteristic of the EPR spectrum of trivalent titanium complexes [10,11]. The observed EPR spectra of trivalent titanium ions in the crystal field of axial symmetry exhibit the following values of the g -factor: $g_1=1.971(1)$ and $g_2=1.940(1)$. These values are attributed to the rutile phase of TiO_2 [12].

Fig. 2A presents the temperature dependence of the EPR integrated intensity I_{int} for all test systems. The integrated intensity was calculated as the area under the absorption spectra. At low temperatures (below 45K), the temperature dependence of reciprocal I_{int} shows a Curie-type behaviour for all

**Fig. 1.** EPR spectra of sample 3 (top) and 4 (bottom) at different temperatures.

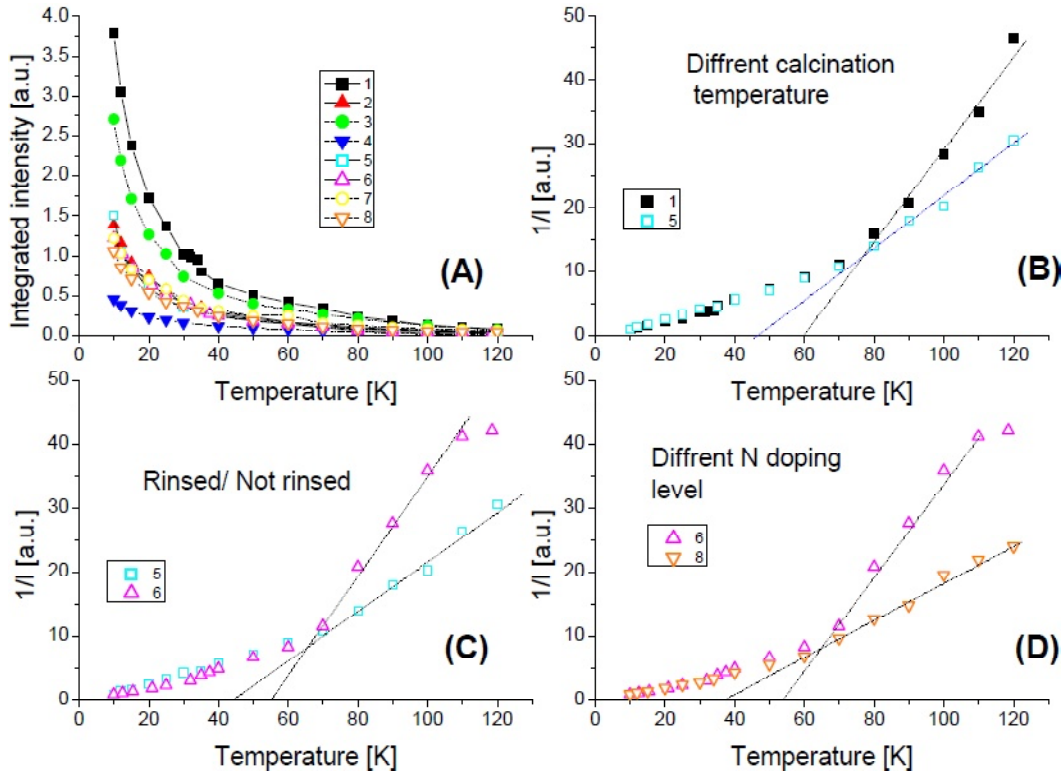


Fig. 2. Temperature dependence of integrated intensity for all samples (A), and temperature dependence of reciprocal of integrated intensity for samples 1 and 5 (B), samples 5 and 6 (C), and samples 6 and 8 (D).

samples. In the high temperature region ($T > 50\text{K}$), nevertheless, it exhibits a different behaviour. At $T > 50\text{K}$ a Curie-Weiss-type function, $I_{\text{int}} = C / (T - \theta)$, where θ is the Curie-Weiss temperature, was used successfully to describe the $I_{\text{int}}(T)$ dependence. The obtained values of θ are positive for all systems, which indicates the presence of dominating ferromagnetic interactions between paramagnetic centers. The value of θ (and hence the strength of ferromagnetic interaction) depends crucially on the type of TiO_2 modification. Figs. 2B-2D depict the way a particular type of modification changes the value of the Curie-Weiss temperature. In particular, Fig. 2B presents the influence of different calcination temperatures (750/800 °C) on θ . It is evidenced that sample 1, calcined at lower temperature, exhibits a higher Curie-Weiss temperature ($\theta = 60\text{K}$) than sample 5 ($\theta = 45\text{K}$), calcined at higher temperature. In Fig. 2C the effect of rinsing with water is demonstrated. Rinsing increases the value of θ , from $\theta = 45\text{K}$, for the non-rinsed sample 5, to $\theta = 55\text{K}$ for the rinsed sample 6. The consequence of different N doping level is presented in Fig. 2D. Sample 6, subjected to low level of N doping, has a greater Curie-Weiss temperature than sample 8 ($\theta = 35\text{K}$), which was strongly N doped. It can be deduced, therefore, that higher temperature of calcination and higher level of N doping decreases the

Curie-Weiss temperatures and, in consequence, the strength of ferromagnetic interaction. On the other hand, water rinsing increases ferromagnetic interactions.

The strength of ferromagnetic interaction is closely connected with the concentration of the free electrons participating in electric conductivity. Above 45K the concentration of conducting electrons increases with increasing temperature and the skin effect begins to play an important role in the determination of the EPR signal intensity. In particular, the skin depth (δ) is related to the electrical conductivity (σ), according to the equation: $\delta = 2 / \mu_0 \omega \sigma$, where ω is the frequency of the electromagnetic waves. The EPR integrated intensity is also strongly dependent on the electrical conductivity according to the following relation [13]: $I_{\text{int}} \sim \{2\exp(-w) + [1 + \exp(2w)] / w\} / [1 + \exp(-w)]^2$, where $w = d / \delta$ (d is thickness of the conducting sample). It was shown previously that transport processes in dioxide titanium could be explained by small polaron conduction, in the high temperature regime, and by Mott variable range, hopping at lower temperatures [14].

4. CONCLUSIONS

In summary, EPR measurements have revealed that an increase of electric conductivity in dioxide tita-

nium is evidenced by an increase of the observed ferromagnetic interactions. Some modifications of TiO₂ cause a reduction in ferromagnetic interaction strength (higher calcination temperature and higher level of N doping), while water rinsing intensifies this interaction. Finding specific preparation modifications of TiO₂ can lead to the preparation of suitable correlated spin systems for applications in future spintronics.

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