

Appearance of itinerant electrons detected by IR spectroscopy and its correlation with surface magnetism in Co-doped TiO₂ nanopowders

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Abstract. IR absorption and magnetic data for the titanium dioxide nanopowders are studied. Additional absorption in IR range is revealed in nanocrystalline TiO₂ and Co-doped TiO₂ after reducing annealing and explained by appearance of the oxygen vacancies and delocalised charge carriers. Increasing of the absorption in IR range after annealing of Co-doped TiO₂ in vacuum (or decreasing of this contribution after annealing in air) correlates with arising (or vanishing) of ferromagnetic contribution.

1 Introduction

Titanium dioxide in nanostate is one of the intensively studied materials for nanotechnology applications in photocatalysis and photoelectrochemical solar cells, in sensors, spintronics, and medicine [1]. Various reducing treatments, creation of the oxygen vacancies, doping by 3d ions modifies the electronic and magnetic properties of nano-TiO₂ and this is the way for improvement of the properties which are important for practice.

Recently it was shown that doping TiO₂ with Co-ions up to 4% and subsequent annealing in vacuum at 1000 K results in appearance of spontaneous magnetization at room temperature that was associated with the increase in the Co atoms content on the surface of nanoparticles [2]. The results were interpreted within the framework of core-shell model. It was assumed that the ferromagnetic ordering is a result of the interaction of delocalized electrons near the vacancies and the nearest neighbour cobalt atoms due to itinerant type interaction. One of the methods that can answer the question about the existence of the delocalized states in semiconductor is the infrared spectroscopy and study of the absorption spectra in the “transparency window” between the fundamental and phonon absorption where delocalised charge carriers can manifest themselves. In the present work we try to establish the relation between the evolution of the magnetic properties and IR spectra in Co-doped TiO₂ nanopowders under the reducing treatment as well. To separate influence of the Co-doping and different treatments on the evolution of the IR spectra of the titanium dioxide the absorption data of undoped nanocrystalline TiO₂ were studied also.

2 Experimental details

Nanocrystalline TiO₂ and TiO₂:Co (Co content is 1.5 at%) were prepared by the hydrothermal method [2]. XRD indicates the formation of anatase structure. The size of the nanoparticles determined by TEM is about 60–80 nm in length and 20–25 nm in width.

Before any measurements and annealing the treatment of the synthesized TiO₂ and TiO₂:Co nanopowders in HCl was carried out to remove contamination on the surface, if any. These powders are denoted as the nanopowders in initial state. Then the reducing annealing was carried out in vacuum of 10⁻⁴ Pa at T~1000 K during 30 minutes. Further, one part of the vacuum treated nanopowders was annealed in air at 670 K during 2 hours and another part was again etched in HCl.

Magnetization of the nanocrystalline TiO₂:Co was measured at room temperature on the Faraday balance in the fields up to 12 kOe.

For the optical measurements nanopowders of TiO₂ or TiO₂:Co were compacted with CsI under the pressure P=5 GPa. To study the evolution of the IR absorption of TiO₂ or TiO₂:Co nanopowders the transmission of the obtained composites in the range 0.9-12.5 μm was measured and optical density was calculated as $D(\lambda)=\ln(1/T(\lambda))$. The transmission spectrum of CsI was taken into account.

3 Results and discussion

Figure 1 demonstrates the magnetization curves of the nanocrystalline TiO₂:Co. It is shown that initial TiO₂:Co nanopowder is paramagnetic. After annealing of the nanopowder in vacuum behaviour of the magnetization curve changes drastically, and the ferromagnetic contribution is clearly observed. Saturation magnetization M_s at T=300 K is about 0.85 emu/g. Subsequent annealing of the TiO₂:Co powder in air

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results in decreasing of the magnetization, but $M(H)$ curve still demonstrates ferromagnetic-like character: the saturation of M is observed, the value of M_s is about 0.04 emu/g (the insert in Figure 1).

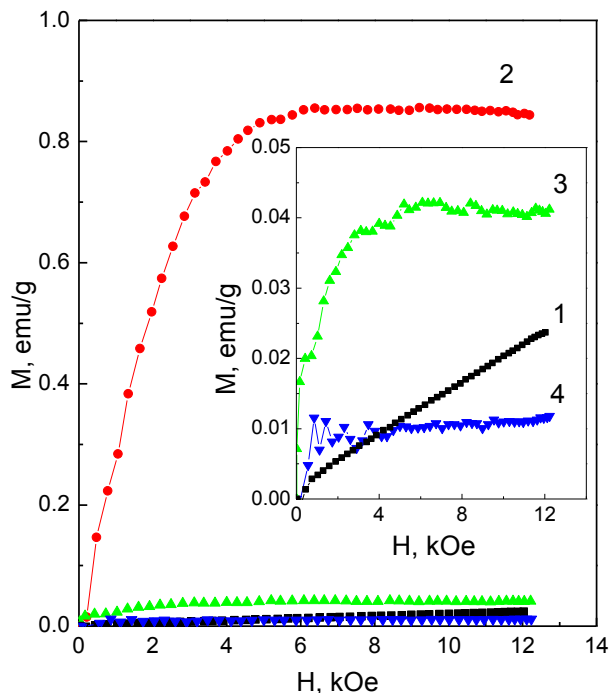


Fig. 1. The magnetization curves for $\text{TiO}_2\text{:Co}$ nanopowders. 1 – initial state, 2 – annealing in vacuum, 3 – annealing in vacuum and further annealing in air, 4 – annealing in vacuum and etching in HCl.

HCl-etching $\text{TiO}_2\text{:Co}$ nanopowder annealed in vacuum affects magnetization more significantly than the annealing in air. The curve $M(H)$ becomes close to that of initial powder $\text{TiO}_2\text{:Co}$. Disappearing of the magnetization after etching in HCl is in agreement with the conclusion made in [2] that there is the tendency of

Co-ions to localise on the surface and subsurface layers resulting in increase in the Co atoms content there as compared with that in the bulk.

The optical density spectra $D(\lambda)$ of $\text{TiO}_2\text{:Co}$ nanopowders in comparison with that of undoped TiO_2 are presented in Figure 2. $D(\lambda)$ curves for the powders with and without Co-ions have the same character. The increase of the absorption in the long-wave range of the spectra is associated with the phonon band with the frequency $\nu_{\text{LO}}=876 \text{ cm}^{-1}$ ($\lambda=11.41 \text{ }\mu\text{m}$) [3]. The increase of the absorption in the shortwave range of the spectra is caused by the presence of the band at $\lambda\sim 1 \text{ }\mu\text{m}$ ($E\sim 1.2 \text{ eV}$) associated with the polaron optical absorption due to self-trapped electrons undergoing hopping between Ti^{4+} and Ti^{3+} [4]. In $D(\lambda)$ spectra of the powders in the initial state there are the weak absorption bands at $\lambda=7.3 \text{ }\mu\text{m}$, $6.2 \text{ }\mu\text{m}$, and $3.1 \text{ }\mu\text{m}$ which correspond to the vibrations of b-CO_3 , water, and O-H strongly adsorbed on the nanoparticles surface [5]. Doping with Co does not influence the spectra at $\lambda>4 \text{ }\mu\text{m}$ and results in the increase of the absorption at $\lambda<4 \text{ }\mu\text{m}$ that is caused by the appearance of the absorption bands attributed to the d-d- transitions in Co-ions [6].

After annealing of nanopowders in vacuum, the following evolution of the optical spectra occurs. The bands at $\lambda=7.3 \text{ }\mu\text{m}$, $6.2 \text{ }\mu\text{m}$, and $3.1 \text{ }\mu\text{m}$ are almost disappeared, that can be explained by removal of the corresponding molecules from the nanoparticles surface. The absorption increases both for undoped and Co-doped titanium dioxide (curves 2 in Fig.2). The growth of the absorption in the short-wave range is the result of the appearance additional absorption band at $\sim 0.8 \text{ }\mu\text{m}$ attributed to Ti^{3+} ions [8].

The more intriguing change of $D(\lambda)$ spectra is observed near phonon bands. The increase of the absorption near phonon edge begins at shorter wavelength (at $\lambda\sim 7 \text{ }\mu\text{m}$) and $D(\lambda)$ curves in the range $\lambda>7 \text{ }\mu\text{m}$ is turned up in contrast to the curves of the powders in initial state, that is typical for materials with delocalised charge carriers. It is known that the higher

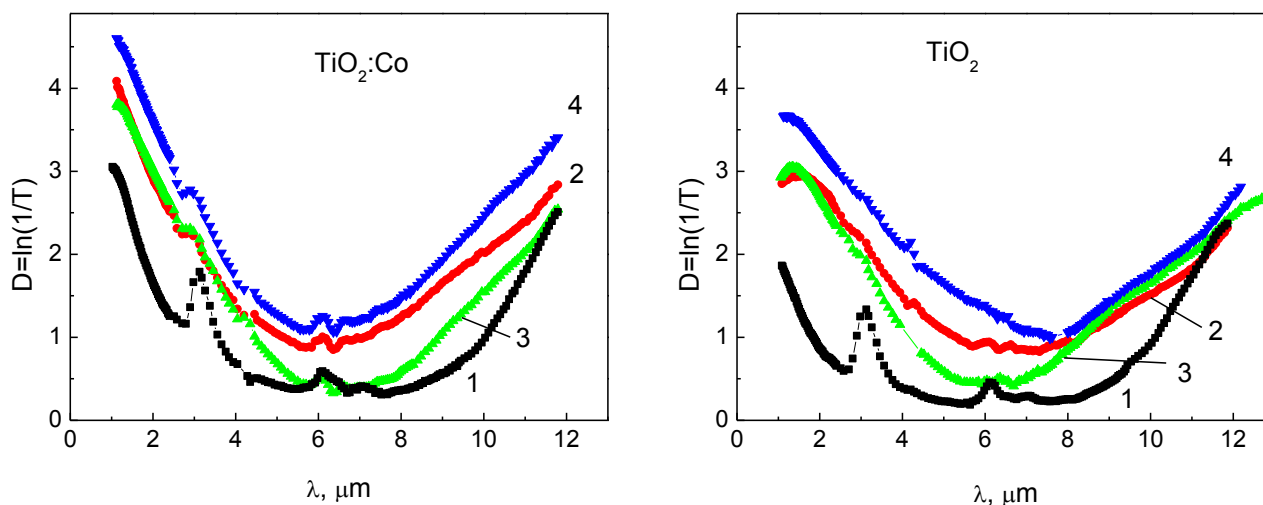


Fig. 2. Optical density spectra of $\text{TiO}_2\text{:Co}$ (a) and TiO_2 (b) nanopowders. 1 – initial state, 2 – annealing in vacuum, 3 – annealing in vacuum and further annealing in air, 4 – annealing in vacuum and etching in HCl

conductivity of the material corresponds to the higher absorption coefficient in IR range. It is important that delocalised charge carriers appears not only in TiO₂:Co powder but in undoped TiO₂ too. Therefore, the origin of these carriers is not connected with the possible appearance of the droplets of metallic Co on the nanoparticles surface. So, the growth of the absorption and the appearance of Drude-like additional contribution in D(λ) spectra may be explained by appearance of delocalised charge carriers associated with the oxygen vacancies.

Annealing reduced TiO₂ or TiO₂:Co nanopowders in air results in decrease of the absorption (curves 3 in Fig.2), but some residual Drude-like contribution remains. It means that some amount oxygen vacancies still remains. Decrease of the absorption of nanopowders after annealing in air correlates with the decrease of the magnetization (Fig.1) and is in agreement with the hypothesis about itinerant type of magnetism [2].

As one can see, if nanopowder contains Co-ions, change of the absorption after the reducing or oxidizing annealing is somewhat stronger than that for undoped TiO₂. One of the possible reasons is that doping TiO₂ with cobalt is accompanied by a significant increase in the concentration of the oxygen vacancies, as it was shown by study of the electron paramagnetic resonance [2]. Another reason may be so that segregations of Co-ions on the surface of the nanopowder after annealing in vacuum may lead to some segregation of the delocalised charge carriers. As a result, their contribution into the optical spectra is stronger.

Now let us consider the influence of HCl etching TiO₂ or TiO₂:Co nanopowders annealed in vacuum on the optical density spectra. Although the magnetization of TiO₂:Co after HCl-etching decreases more strongly than after annealing in air, the absorption does not decrease (curves 4 in Fig.2) but even slightly increases. It again indicates that delocalised charge carriers do not appear from the metallic Co-droplets, if any. The distinction in the influence of HCl-treatment on the magnetic and optical properties may be explained by the difference of the thickness of surface layer of nanoparticles, in which the charge carriers connected with oxygen vacancies appear or the magnetization is formed.

4 Conclusions

We have reported the IR absorption data (optical density spectra D(λ)) of nanocrystalline TiO₂:Co and TiO₂ after different heat treatment and etching in HCl.

In the optical density spectra of TiO₂ and TiO₂:Co nanopowders after annealing in vacuum an additional absorption of Drude-like character appears. It is revealed that there is the correlation between the appearance and disappearance of the ferromagnetic-like magnetization and Drude-like contribution after reducing or oxidizing annealing, respectively. It is shown that Drude-like contribution is not connected with possible forming of metallic Co-rich droplets. The results support the

hypothesis about itinerant type of surface magnetism in Co-doped TiO₂ nanopowders.

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References

1. X. Chen, Chin. J. Catal., **30**, 839 (2009).
2. A.Ye. Yermakov, G.S. Zakharova, M.A. Uimin et al., J. Phys. Chem. C **120**, 28857 (2016)
3. R. J. Gonzalez, R. Zallen, and H. Berger, Phys.Rev.B **55**, 7014 (1997)
4. C. A. Triana, C. G. Granqvist, and G. A. Niklasson, J. Appl. Phys. **119**, 015701 (2016)
5. C. Yan, W. Yi, H. Yuan, et al, Environmental Progress & Sustainable Energy **33**, 419 (2014)
6. B. Babu, Ch. Rama Krishna, Ch. Venkata Reddy et al., Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy **109**, 90 (2013)
7. V.N. Kuznetsov and N. Serpone, J. Phys. Chem. C, **113**, 15110 (2009)