Structural and magnetic properties of mechanochemically synthesized nanocrystalline titanium monoxide

Tanja Barudžija*[a], Marija Perović[a], Vojislav Spasojević[a], Miroslav Dramićanin[a], Čeda Jovalekić[b], Miodrag Mitrić[a]

[a] *Vinca Institute, Belgrade, Serbia, tbarudzija@vinca.rs*
[b] *Centre for Multidisciplinary Studies, Belgrade, Serbia, jovalek@ibiss.rs*

Abstract
Nanosized titanium monoxide, TiO powders were prepared by mechanically assisted synthesis. A mixture of commercial Ti and TiO_2 (anatase) powders with molar ratio of 1:1 was milled for 0.5 and 1 h under nitrogen atmosphere. The samples were further characterized by XRD, SQUID measurements and by thermo gravimetric analysis (TGA). The temperature dependency of the magnetic susceptibility is characterized by the significant contribution from the Pauli paramagnetism due to conduction electrons.

Experimental and results

Titanium monoxide was prepared using the mechanochemical treatment. A mixture of commercial Ti and TiO_2 (anatase) powders with molar ratio of 1:1 was used as the starting material. Mechanochemical treatment was performed in a planetary ball mill (Fritsch Pulverisette 7) in nitrogen atmosphere. A tungsten carbide vial of 45 ml volume filled with 144 tungsten carbide balls of 5 mm diameters. Balls to powder weight ratio was 20:1. The angular velocity of the supporting disc and vial was 104.7 rad s^{-1} (1000 rpm). After selected milling times (30 and 60 min) the samples of powder were taken for X-ray diffraction measurements (Philips PW 1050 powder diffractometer with Ni filtered Cu$K\alpha$ radiation and scintillation detector) within 10−70° 2θ range in steps of 0.05°, and scanning time of 2 s per step. After XRD measurements, the powder was placed back in a vial to obtain the same grinding conditions (balls to powder weight ratio). For Rietveld's refinement XRD measurements were done within 25−135° 2θ range in steps of 0.02°, and scanning time of 14 s per step. The XRD pattern of the TiO was analyzed by the Rietveld profile method assuming the space group Fm-3m.

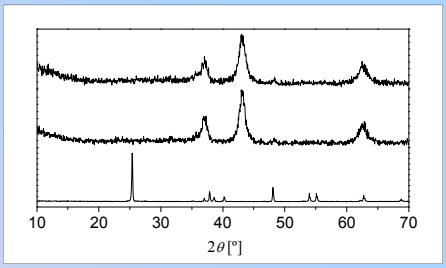
Magnetic measurements were done by using Quantum Design MPMS SQUID magnetometer. ZFC measurements were carried out in the temperature range of 10–300 K, and in applied fields of 2000 and 5000 Öe. Measurements of the magnetization M were recorded in magnetic fields with a strength H up to 50 kÖe and at temperatures of 4 and 300 K.

The dependence $\chi(T)$ for titanium monoxide is well described by the function:

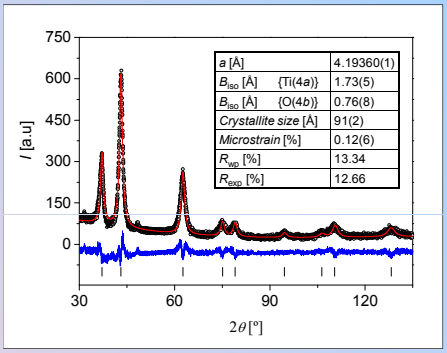
$$\chi(T) = \chi(0) + \frac{C}{T+\Delta} + bT^2 , \qquad (1)$$

where $\chi(0)$ is the temperature-independent paramagnetic contribution, C is the Curie constant, Δ is Curie temperature and the quadratic term bT^2 is characteristic of the Pauli paramagnetism due to conduction electrons. The fitting parameters of equation (1) are presented in table.

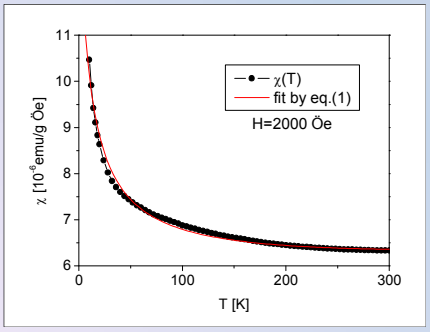
H [Öe]	$\chi(0)$ [10^{-6}emu/g Öe]	C [10^{-6}emu/g Öe K]	Δ [K]	b [10^{-12}emu/g Öe K^2]
2000	5.98(1)	90(2)	11.7(6)	1.1(2)
5000	4.33(1)	82(2)	8.6(5)	0.29(6)



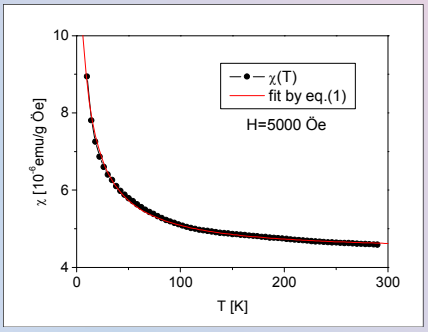
XRD patterns of the mixture of Ti and TiO_2 powders with molar ratio of 1:1 milling for 0, 30 and 60 min.



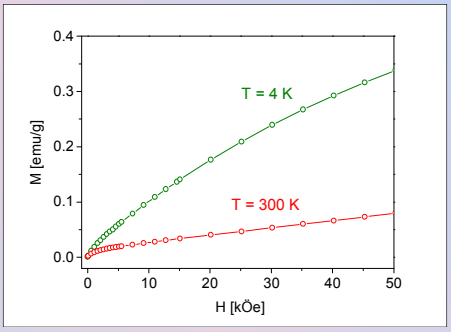
Comparation of observed (circles) and calculated (solid red line) intensities. The differences between the observed and calculated intensities (solid blue line). The vertical bars indicate the Bragg peaks.



Magnetic susceptibility within 10−300 K range of titanium monoxide in applied field of 2000 Öe fitted by eq. (1)



Magnetic susceptibility within 10−300 K range of titanium monoxide in applied field of 5000 Öe fitted by eq. (1)



Simultaneous TGA/DTA measurements were carried out up to 900 °C in the air atmosphere at a heating rate of 20°C min^{-1} using the thermobalance TA SDT Model 2090. The Ti:O ratio was determined from the mass increase during the oxidation to TiO_2 and suggested composition of mechanochemically synthesized titanium monoxide is $TiO_{1.03}$. The oxygen content was higher than expected from the composition of starting mixture.