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Hydrothermal synthesis and characterization of rod-like co-doped anatase for spintronic applications

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Nanopowders based on Co-doped TiO_2 anatase with homogeneous distribution of doping agents were obtained by kinetic controlled hydrothermal process in the presence of KOH as mineralizing agent. The rod-like structure may be explained by the formation in the initial phase of Potassium Hydrogen Titanium Oxide Hydrate that transforms with further increasing of hydrothermal treatment time to more stable anatase. The EPR investigations show two ferromagnetic behaviors: in the low temperature range 110-160K, the evaluated Curie temperature θ value is 110K while in the high temperature range 170-230K a value of 165K is obtained. The results support the great potential for further applications in spintronics.

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1. Introduction

Diluted magnetic semiconductor oxides (DMO) based on Co-doped TiO_2 (CTO) materials have received a high interest due to their ferromagnetic properties with high potential in spintronic applications [1-4]. The origin of ferromagnetism in CTO materials is strongly dependant on doping concentration and distribution and the presence of lattice defects such as oxygen vacancies. Consequently obtaining of nanopowders allowing stabilization of non-equilibrium phases is expected to strongly influence the ferromagnetic and spin dynamics properties of these materials [5]. Different chemical or physical methods have been reported for the synthesis of pure and doped TiO_2 nanomaterials with different morphologies [6]. Hydrothermal synthesis is one of the methods enabling to produce nanopowders in one step process at low temperatures from a wide range of soluble or amorphous precursors. However prediction and selection of optimal pH range, temperature, duration and mineralizing agents controlling both powders morphology and Co distribution is a challenge [7-9].

In the present paper the kinetic control of hydrothermal process in alkaline media was used for the first time to obtain TiO_2 anatase nanopowders homogeneous doped with controlled Co content having a rod-like structure. The electron paramagnetic resonance (EPR) spectra of the as-synthesized nanopowders demonstrate the ability of the proposed method to obtain materials with controlled properties for spintronic applications.

2. Materials and experimental methods

High purity titanium (IV) chloride, cobalt acetate $Co(CH_3COO)_2.2H_2O$, ammonia solution 25% and potassium hydroxide pellets were used in the synthesis. Firstly an aqueous solution with controlled concentration of Ti(IV) ions was obtained by dissolution of Ti(IV) chloride under stirring in distilled water in the presence of hydrogen peroxide (H_2O_2). Cobalt acetate was also dissolved in distilled water under stirring to get a solution with controlled Co (II) concentration. The two solutions were mixed in a volume ratio to obtain a mixed solution with 2.5 and 5 at % Co respectively. The pH of the solution was then adjusted to the desired experimental value by addition of both ammonia and KOH and the suspension was treated in a CORTEST Teflon autoclave at different temperatures and times. The final precipitate was filtered, washes with water several times to eliminate soluble impurities and dried in an oven to constant weight.

Chemical analysis of all initial solutions and final powders was accomplished by Atomic absorption spectrometry (AAS ZEEnit 700, Analytic Jena AG) and Indirect Plasma Coupled Spectrometry (ICP Spectroflame). Phase analysis was carried out by XRD (Bruker D8 Advance) using CuK_α radiation with the help of DIFFRAC^{plus} BASIC (Bruker AXS) software and ICDD PDF-2 Release 2006 database. A small amount of powder was diluted into pure ethylic alcohol and left into an ultrasonic bath for approximately 15 minutes. After that, a small drop of the diluted solution was put onto a 400 mesh, holey carbon coated film Cu grid and left to dry for 30 minutes, prior to TEM investigation. The bright field and high resolution images were obtained using a Tecnai^{TM} G^2 F30 S-TWIN Transmission Electron

Microscope (FEI, the Nederlands), equipped with a STEM/HAADF detector, EDX (Energy Dispersive X-ray analysis) and EFTEM-EELS spectrometer (Electron Energy Loss Spectroscopy). Electron paramagnetic resonance (EPR) measurements of powder samples were carried out in the X-band at variable temperature using a Bruker E-500 ELEXSYS spectrometer in the temperature range 110-290K.

3. Results and discussion

The chemical composition and length/width ratio of the particles vs. experimental conditions for the synthesis of nanostructured Co-doped powder are briefly presented in Table 1.

Table 1. Chemical composition and aspect ratio of Co-doped nanoparticles vs. hydrothermal synthesis parameters.

Sample code	T [^{0}C]	Time [s]	Length [nm]	Width [nm]	Ratio L/W	Co [at%]	K [at%]
2.5CoTi-T1	250	10	63.21	11.51	5.49	2.48	5.56
2.5CoTi-T3	250	20	57.13	11.45	4.99	2.35	1.08
2.5CoTi-T4	250	40	68.61	16.41	4.18	2.13	0.79
2.5CoTi-T6	250	60	55.61	16.2	3.43	2.04	0.14
5CoTi-T1	250	10	58.5	11.45	5.11	5.75	5.29
5CoTi-T3	250	20	55.52	11.55	4.81	4.09	1.28
5CoTi-T4	250	40	59.78	13.05	4.58	4.97	1.19
5CoTi-T6	250	60	79.12	15.65	4.06	6.90	0.15

All samples show that pure anatase powders were formed. The evolution of the major characteristic peak [101] from the XRD pattern of 5at% Co-doped anatase powders is shown in Fig. 1. XRD pattern of anatase powders doped with 2.5 at% Co has a similar aspect.

The size and morphologies of powders doped with 5at%Co synthesized at 250 ^{0}C after 20 min is revealed by TEM bright field image obtained on 5CoTi_250_T3 sample shown in Fig. 2 reveals that the powder is composed from rod like particles, with an average grain size of approximately 55.52 nm in length and 11.65 in width.

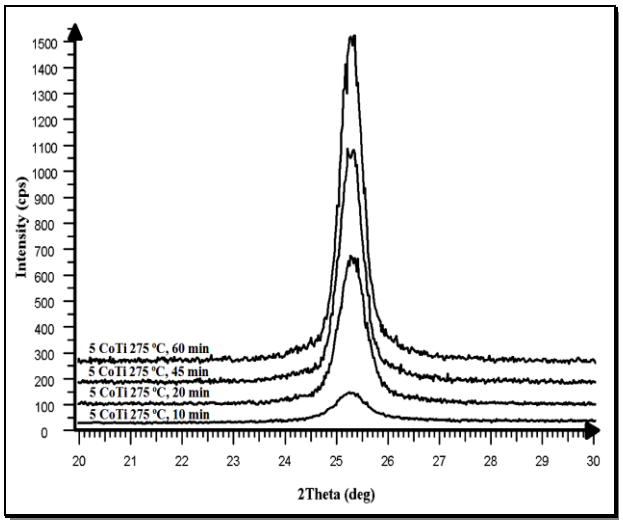

Fig. 1. The evolution of characteristic peak [101] of 5 at% Co-doped anatase synthesized at 275^{0}C vs. reaction time.

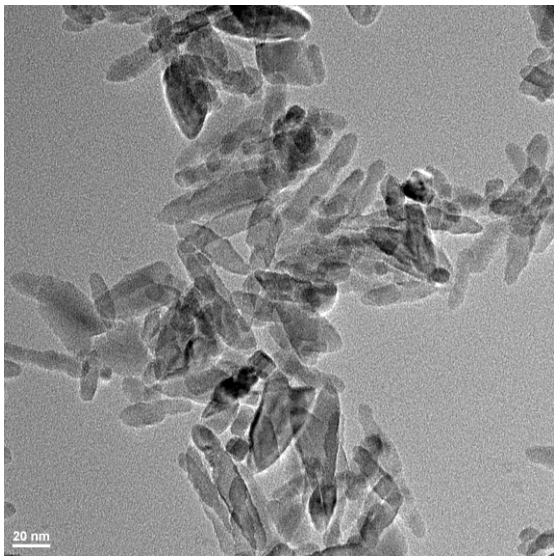

Fig. 2. Bright field TEM image of 5CoTi-250-T3 sample.

The HRTEM image obtained on the same sample is shown in Fig. 3. The image shows clear lattice fringes of polycrystalline nanopowder of d = 3.51 and 2.37 Å corresponding to the (1 0 1) and (0 0 4) crystallographic planes of TiO_2 anatase. Also the regular succession of the atomic planes indicates that the nanocrystalites are structurally uniform and crystalline with almost no amorphous phase present. From the selected area diffraction pattern obtained presented in Fig. 3 b we can state that the only phase identified is the polycrystalline tetragonal phase of TiO_2 anatase.

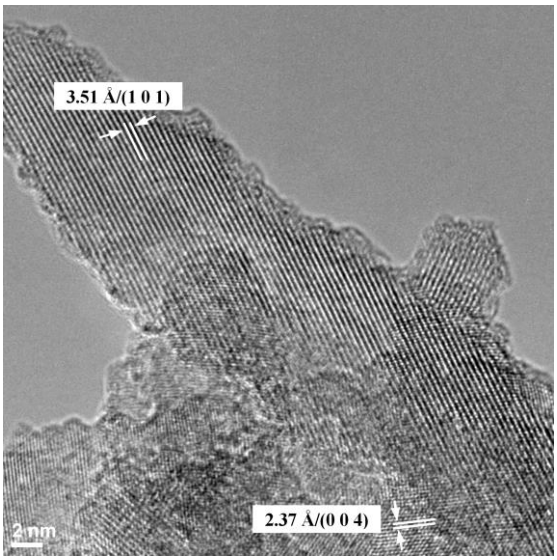

Fig. 3(a). HR-TEM image of sample5CoTi-250-T3.

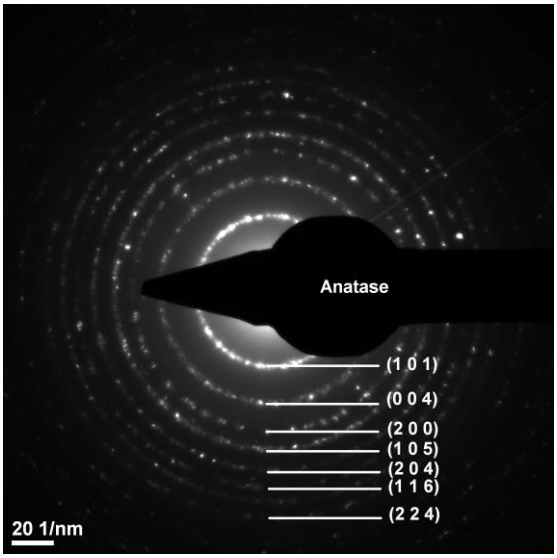

Fig. 3(b). SAED image of sample 5CoTi-250-T3.

The formation of rod-like structure may be explained due to the formation in the initial phase of Potassium Hydrogen Titanium Oxide Hydrate $K_{0.48}H_{0.22}Ti_{1.825}O_4(H_2O)_{0.52}$ (lattice parameters a=3.7896 Å, b=17.908 Å, c=2.9854 Å) that was identified both by XRD and HREM (not shown here) in the initial stages of the process (the inter-planar distances d = 1.94 Å corresponding to crystallographic plans (0 7 1) could be clearly identified). With further increasing of hydrothermal treatment time this phase transforms to more stable anatase as seen in the Table 1.

The experimental EPR spectra recorded at some selected temperature for the sample 5CoTi275 is presented in Fig. 4.

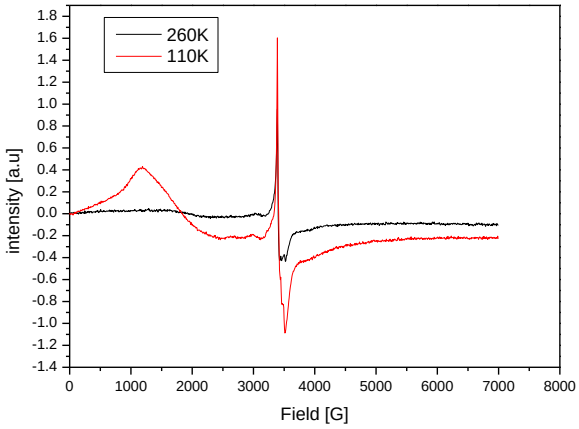

Fig. 4. EPR spectra recorder at two selected temperatures for 5CoTi275T6.

The analysis of the spectra shows two signals, one near 2000G and the other 3100 G. These signals correspond to the Co^{2+} ions having the effective $g_{\perp}$ = 3.285 and $g_{//}$ = 2.198, respectively. The sharp line situated at 3400 G could be attributed to the effect centers implying Ti^{3+} ions. Also we observe that by increasing temperatures the Co ions signal is decreasing due to the very high relaxation time. For samples doped with 5at% Co our EPR investigations show two ferromagnetic behaviors as function of temperature. In the low temperature range 110-160K, the evaluated θ value is 110K while in the high temperature range 170-230K a value of 165K is obtained. It could means that at higher temperatures the exchange interaction between Co ions increases leading to an increase of the Curie-Weiss temperature.

4. Conclusions

Co-doped TiO_2 nanopowders with 100% anatase structure were prepared using hydrothermal synthesis. The control of the kinetic process in the presence of controlled amounts of KOH used as mineralizing agent. Nanopowders with homogenous distribution of Co doping element and rod-like structure were produced. The EPR investigations show two ferromagnetic behaviors: in the low temperature range 110-160K, the evaluated Curie temperature θ value is 110K while in the high temperature range 170-230K a value of 165K is obtained. The results support the potential for further applications in spintronics.

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References

[1] A. K. Pradhan, D. Hunter, B. D. Hunter, J. B. Dadson, K. Zhang, R. R. Rakhimov, J. Appl. Phys. **99**, 08M108-1-3 (2006).
[2] M. Bibes, M. Bowen, A. Barthelemy, A. Anane, K. Bouzehouane, C. Carratero et al. Appl. Phys. Lett. **82**, 3269 (2003).
[3] Y. G. Joh, H. D. Kim, S. I. Woo, S. H. Moon, J. H. Cho, E. C. Kim, et al. J. Appl. Korean Phys. Soc. **44i**, 360 (2004).
[4] N. N. Hai, N. T. Khoi, P. V. Vinh, J. Phys: Conf. Series. **187**, 1(2009).
[5] L. C. J. Perreira, M. R. Nunes, O. C. Monteiro, A. J. Silvestre, Appl. Phys. Lett. **93**, 222502-1-222502-3 (2008).
[6] X. Chen, S. S. Mao, Chem. Rev. **107**, 2891 (2007).
[7] M. Abrudeanu, R. R. Piticescu, R. M. Piticescu, Bucharest: Editura Tehnica; 68-80 (1999).
[8] D. L. Morgan, H. W. Liu, R. L. Frost, E. R. Waclawik, J. Phys. Chem. C **114**, 101 (2010).
[9] R. M. Nunes, O. C. Monteiro, A. L. Castro, D. A. Vasconcelos, A. J. Silvestre, Eur. J. Inorg. Chem. 961 (2008).

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