



Upconverting Ho–Yb doped titanate nanotubes

M. Pedroni ^a, F. Piccinelli ^a, S. Polizzi ^b, A. Speghini ^a, M. Bettinelli ^a, P. Haro-González ^{a,c,*}

^a Laboratorio di Chimica dello Stato Solido, DB, Università di Verona and INSTM, Udr Verona, Ca' Vignal, Strada Le Grazie 15, I-37134 Verona, Italy

^b Dipartimento di Scienze Molecolari e Nanosistemi, Università Ca' Foscari Venezia and INSTM, Udr Venezia, Via Torino 155/b, 30172, Venezia - Mestre, Italy

^c Departamento de Física Fundamental y Experimental, Electronica y Sistemas, Universidad de La Laguna, Av. Astrofísico Francisco Sanchez, s/n, 38206, La Laguna, Spain

ARTICLE INFO

Article history:

Received 24 January 2012

Accepted 21 April 2012

Available online 26 April 2012

Keywords:

Nanotubes

Spectroscopy

FTIR

X-ray diffraction

Titanate

Upconversion

ABSTRACT

The synthesis of Ho³⁺–Yb³⁺ codoped titanate nanotubes was carried out successfully via a hydrothermal treatment method from a precursor powder. These novel nanotubes treated at RT, 100 °C and 280 °C were studied with the aim of determining their structural and optical properties. As the thermal treatment was increased, their upconversion emission becomes stronger. This behavior was related to reduction of hydroxyl groups and the water on the surface, which resulted in changes in the interlayer distances of the nanotubes.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Nano-structured optical materials have attracted great attention due to their potential applications in high-performance photonic and bio-photonic fields [1–3]. Among these materials, rare earth (RE) doped nanomaterials are widely investigated due to excellent luminescence characteristics arising from 4f–4f transitions [2], giving rise to long luminescence lifetimes and low absorptions, which have clear advantages in applications of lasers, optical amplifiers and phosphors [4–6].

Nanotubes structure has attracted recently increasing interest [7,8] for its unique combination of shape and functionality where, in the ideal case, materials properties may be directly influenced by the 1D-nanoscale nature of the geometry [7].

While by far most efforts in contemporary nanotubes research and technology address carbon based nanotubes [9,10], nanotubular materials based on transition metal oxides are gaining steadily increasing momentum. Titanium dioxide has been extensively studied due to its important properties and application. This material not only has shown excellent photo-catalytic and magnetic properties [10], also it has been considered to be a potential host for lanthanide ions because of their low-cost and high transparency in the visible wavelength region as well as good thermal, chemical, and mechanical properties [11,12]. The synthesis of titanate nanotubes has been successfully obtained by a great variety of methods [13–16].

Few works have been published on RE-doped titanate nanotubes and their photoluminescence properties. B. Chi et al. [17] obtained Eu³⁺-doped titanate nanotubes with strong emission lines. J. Yin et al. [18] reported the luminescence properties of Eu³⁺-doped titanate nanowires synthesized by sol–gel hydrothermal chemistry. Very recently, our research group presented a study of Eu³⁺-doped titanate nanotubes which exhibited strong red emission [16].

With the aim of extend their potential applications, we present an investigation about novel RE-doped titanate nanotubes doped with Ho³⁺–Yb³⁺ ions. In order to obtain the best upconversion luminescence properties, the nanotubes were treated at different temperatures. Their properties were studied and compared in this letter.

2. Materials and methods

The precursor powders of the titanate nanotubes were obtained by sol–gel method [19]. The starting materials were titanium (IV) butoxide (Aldrich, 97%), Yb(NO₃)₃·5H₂O (Aldrich, 99.9%), Ho(NO₃)₃·5H₂O (Aldrich, 99.9%), absolute ethanol and HCl (37%). In a solution containing 0.8 ml of HCl and 30 ml of ethanol an appropriate quantity of nitrates was dissolved and then 6 ml of titanium (IV) butoxide were added. The solution was stirred for 4–5 h at room temperature (RT). The solvent was evaporated at 50 °C until the xerogel was formed and then the xerogel was heat treated at 500 °C for 5 h. The nominal molar ratios between titanium, holmium and ytterbium ions were 96:2:2.

Titanate Ho³⁺–Yb³⁺ codoped nanotubes were synthesized by hydrothermal method from the precursor powder [16]. 0.5 g of precursor powder was mixed with 80 ml of NaOH 10 M and then transferred into a Teflon vessel and heated at 120 °C for 72 h. After cooling at RT the powder was washed several times with HCl 0.1 M and deionized

* Corresponding author at: Laboratorio di Chimica dello Stato Solido, Strada Le Grazie 15, I-37134 Verona, Italy.

E-mail address: ptharo@ull.es (P. Haro-González).

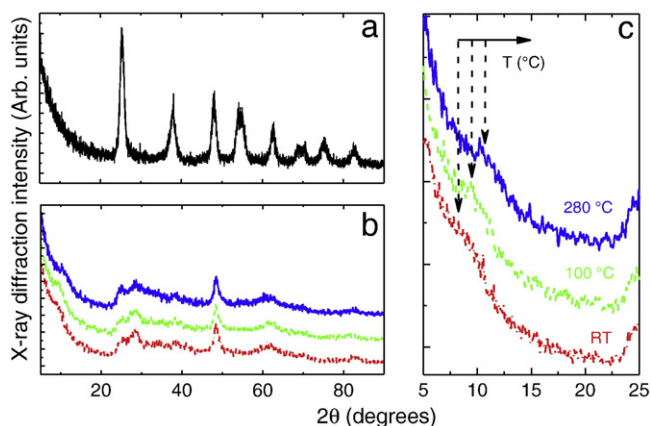


Fig. 1. (a)–XRD pattern of the starting $\text{Ho}^{3+}\text{-Yb}^{3+}$ codoped titanate powder. (b)–XRD pattern of the TiRT (dash-dot line), Ti100 (dash-line) and Ti280 (solid-line) titanate nanotubes. (c)–Detail of the diffraction peaks at 10° .

water until the pH was less than 7 and separated by centrifugation. Finally, the nanotubes were collected and dried at RT for a day. The obtained nanotubes were treated at 100°C and 280°C . These 3 types of nanotubes are labeled TiRT, Ti100 and Ti280.

X-ray powder diffraction (XRPD) data were taken with a Thermo ARL X'TRA powder diffractometer, equipped with a Cu-anode X-ray source (K_{α} , $\lambda = 1.5418 \text{ \AA}$) and a Peltier Si(Li) cooled solid state detector. The patterns were collected with a scan rate of $0.04^\circ/\text{s}$, with measurement times of 1.0 s/step .

Transmission Electron Microscopy (TEM) images were measured using a JEOL 3010, operating at 300 kV , equipped with a Gatan slow-scan CCD camera (model 794). The powders were dispersed in a toluene solution and deposited on a holey carbon film.

RT infrared spectra were measured in the mid infrared region using a Fourier transform infrared (FTIR) spectrometer (Nicolet, Magnet-IR 760) with a spectral resolution of 2 cm^{-1} .

Luminescence measurements were carried out upon excitation with a laser diode at 975 nm . The emission signal was analyzed by a half-meter monochromator (HR460, Jobin Yvon) equipped with a 1200 lines/mm grating and detected with a CCD detector (Spectrum One, Jobin Yvon). The spectral resolution of the emission spectra is 0.1 nm .

3. Results and discussion

The crystal structure of the $\text{Ho}^{3+}\text{-Yb}^{3+}$ codoped nanocrystalline titanate powder used to synthesize the titanate nanotubes was found to be pure anatase (PDF card No. 00-021-1272) (Fig. 1a). The hydrothermal treatment leads to the formation of titanate nanotubes

as evidenced by XRD patterns (Fig. 1b). These patterns are basically the same as those reported previously for this material [16,20,21]. Worth to be mentioning is the behavior of the diffraction peak centered at 2θ almost 10° , attributed to the interlayer diffraction of the titanate nanotubes (Fig. 1c). Increasing the treatment temperature, a shift of the peak toward higher 2θ values is observed. This fact could be ascribed, according to the Bragg law, to a decrease of the nanotube interlayer distance with the increasing of the treatment temperature. TEM images of the nanotubes before and after heat treatment at 280°C , shown in Fig. 2, confirm the X-ray results.

The nature of this change is obviously thermal; therefore the FTIR analysis is advisable. The FTIR spectra were recorded on TiRT, Ti100 and Ti280 titanate nanotubes (Fig. 3a). Some bands are observed in the hydroxyl spectral region ($3000\text{--}3800 \text{ cm}^{-1}$) and these bands change in intensity after heating treatment. The peaks at about 3400 cm^{-1} and 1635 cm^{-1} are due to the stretching vibration of the surface hydroxyl absorption and the bending vibration of the water adsorbed on the surface [22]. The band at 3200 cm^{-1} has a similar behavior as hydrogen-bonded hydroxyl groups on the other oxides and is assigned accordingly. By heating the nanotubes up to 280°C , we observed the decrease of the intensity of the band at $3400\text{--}3200 \text{ cm}^{-1}$, and this behavior is accompanied by the decrease of the band at 1635 cm^{-1} . This is caused by the removal of water from the surface. As a result, the weakening of these bands rise to a change in the nanotubes interlayer distances. The band at 3690 cm^{-1} is assigned to the isolated Ti–OH groups found on titanate nanotubes surface [23].

This behavior has consequences on the luminescence properties; they are sensitive to these changes in the environment of the RE ions. The upconversion emission spectra of the TiRT, Ti100 and Ti280 samples were measured upon excitation the $^2F_{3/2}$ level of the Yb^{3+} ions (Fig. 3b) under the same experimental conditions. They were assigned to $\text{Ho}^{3+}:(^5S_2, ^5F_4) \rightarrow ^5I_8$ (540 nm) and $^5F_5 \rightarrow ^5I_8$ (650 nm) transitions. By obtaining the dependence of the emission intensity with the pump laser power, the number of photon to populate these emitting states are 3 photons (540 nm) and 2 photons (650 nm). As can be seen in the Fig. 3b, when the temperature of the thermal treatment is increased, there is an increment of the upconversion luminescence intensity. It is related directly with the changes described before; the reduction of the hydroxyl groups and the water on the surface, together with the change in the nanotubes interlayer, favors the energy transfer between the Yb^{3+} and Ho^{3+} ions, which produces an increase of the upconversion luminescence intensity.

4. Conclusions

The synthesis of $\text{Ho}^{3+}\text{-Yb}^{3+}$ codoped titanate nanotubes was carried out successfully via a hydrothermal treatment method from

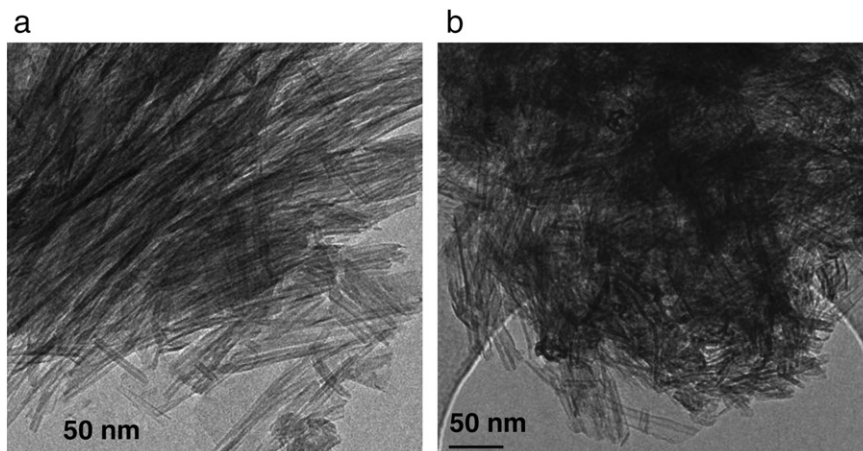


Fig. 2. TEM images of the titanate nanotubes dried at room temperature (a) and heat treated at 280°C (b).

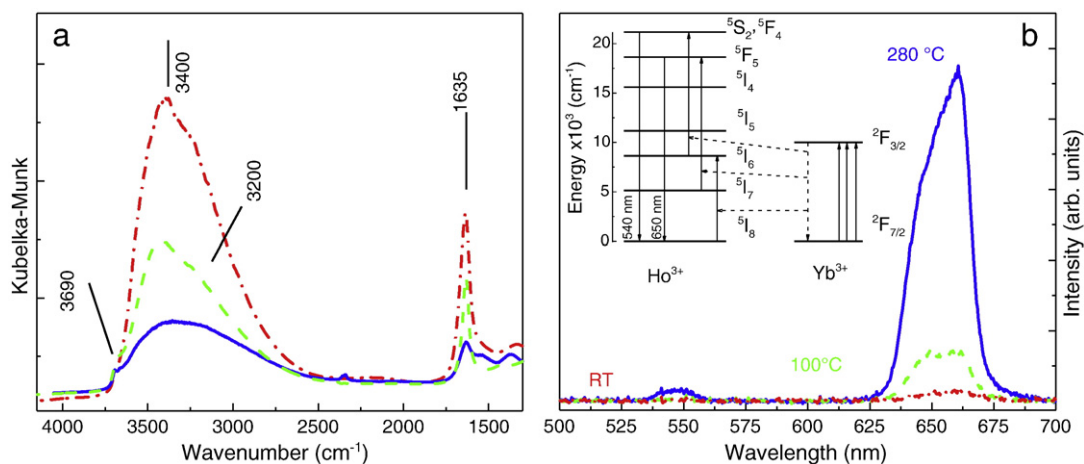


Fig. 3. (a)—FTIR spectra (b)—Upconversion luminescence spectra on TiRT (dash-dot line), Ti100 (dash-line) and Ti280 (solid-line) Ho^{3+} - Yb^{3+} codoped titanate nanotubes.

precursor powder. The nanotubes were obtained at RT and treated at 100 °C and 280 °C. The XRD patterns revealed changes in the nanotubes interlayer distances, produced by the thermal treatment. The FTIR analysis showed the reduction of hydroxyl groups and the water on the surface. As a consequence, the optical properties were affected, giving an increase of the upconversion luminescence.

Acknowledgments

This work was supported by the Fondazione Cariverona, project Verona Nanomedicine Initiative, and by the Spanish Ministerio de Educacion y Ciencia (MAT2010-21270-C04-02).

References

- [1] Kido J, Okamoto Y. Organo lanthanide metal complexes for electroluminescent materials. *Chem Rev* 2002;102:2357–68.
- [2] Chen W, Malm JO, Zwiller V, Huang YN, Liu SM, Wallenberg R, et al. Energy structure and fluorescence of Eu^{2+} in ZnS: Eu nanoparticles. *Phys Rev B* 2000;61:11021–4.
- [3] Erwin SC, Zu LJ, Haftel MI, Efros AL, Kennedy TA, Norris DJ. Doping semiconductor nanocrystals. *Nature* 2005;436:91–4.
- [4] Ren YY, Dong NN, Chen F, Benayas A, Jaque D, Qiu F, et al. Swift heavy-ion irradiated active waveguides in Nd:YAG crystals: fabrication and laser generation. *Opt Lett* 2010;35:3276–8.
- [5] Haro-Gonzalez P, Martin IR, Lahoz F, Gonzalez-Perez S, Cavalli E, Capuj NE. Optical amplification in Er^{3+} -doped transparent $\text{Ba}_2(\text{NaNb}_5\text{O}_{15})$ single crystal at 850 nm. *J Appl Phys* 2009;106.
- [6] Masai H, Fujiwara T, Matsumoto S, Takahashi Y, Iwasaki K, Tokuda Y, et al. White light emission of Mn-doped SnO-ZnO-P(2)O(5) glass containing no rare earth cation. *Opt Lett* 2011;36:2868–70.
- [7] Kuchibhatla SVNT, Karakoti AS, Bera D, Seal S. One dimensional nanostructured materials. *Prog Mater Sci* 2007;52:699–913.
- [8] Mor GK, Varghese OK, Paulose M, Shankar K, Grimes CA. A review on highly ordered, vertically oriented TiO_2 nanotube arrays: fabrication, material properties, and solar energy applications. *Solar Energy Mater Solar Cells* 2006;90:2011–75.
- [9] Iijima S. Helical microtubules of graphitic carbon. *Nature* 1991;354:56–8.
- [10] Iijima S, Ichihashi T. Single-shell carbon nanotubes of 1-Nm diameter. *Nature* 1993;363:603–5.
- [11] Jeon S, Braun PV. Hydrothermal synthesis of Er-doped luminescent TiO_2 nanoparticles. *Chem Mater* 2003;15:1256–63.
- [12] Conde-Gallardo A, Garcia-Rocha M, Hernandez-Calderon I, Palomino-Merino R. Photoluminescence properties of the $\text{Eu}(3+)$ activator ion in the TiO_2 host matrix. *Appl Phys Lett* 2001;78:3436–8.
- [13] Hoyer P. Formation of a titanium dioxide nanotube array. *Langmuir* 1996;12:1411–3.
- [14] Kobayashi S, Hamasaki N, Suzuki M, Kimura M, Shirai H, Hanabusa K. Preparation of helical transition-metal oxide tubes using organogelators as structure-directing agents. *J Am Chem Soc* 2002;124:6550–1.
- [15] Boehme M, Ensinger W. Fabrication of zinc oxide nanotubes by chemical bath deposition using ion track-etched templates. *IEEE Trans Nanotechnol* 2011;10:63–9.
- [16] Haro-Gonzalez P, Pedroni M, Piccinelli F, Martin LL, Polizzi S, Giarola M, et al. Synthesis, characterization and optical spectroscopy of $\text{Eu}(3+)$ doped titanate nanotubes. *J Lumin* 2011;131:2473–7.
- [17] Chi B, Victorio ES, Jin T. Synthesis of Eu-doped photoluminescent titanate nanotubes via a two-step hydrothermal treatment. *Nanotechnology* 2006;17:2234–41.
- [18] Yin JB, Zhao XP. Facile synthesis and the sensitized luminescence of europium ions-doped titanate nanowires. *Mater Chem Phys* 2009;114:561–8.
- [19] Bettinelli M, Speghini A, Falcomer D, Daldosso M, Dallacasa V, Romano L. Photocatalytic, spectroscopic and transport properties of lanthanide-doped TiO_2 nanocrystals. *J Phys Condens Mater* 2006;18:S2149–60.
- [20] Zhang S, Peng LM, Chen Q, Du GH, Dawson G, Zhou WZ. Formation mechanism of $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes. *Phys Rev Lett* 2003;91.
- [21] Nakahira A, Kato W, Tamai M, Ishiki T, Nishio K, Aritani H. Synthesis of nanotube from a layered $\text{H}_2\text{Ti}_4\text{O}_9$ center dot H_2O in a hydrothermal treatment using various titanate sources. *J Mater Sci* 2004;39:4239–45.
- [22] Zou W, Zhang J-L, Chen F, Anpo M, He D-N. A simple approach for preparing a visible-light TiO_2 photocatalyst. *Res Chem Intermed* 2009;35:717–26.
- [23] Dzwigaj S, Arrouel C, Breyse M, Geantet C, Inoue S, Toulhoat H, et al. DFT makes the morphologies of anatase- TiO_2 nanoparticles visible to IR spectroscopy. *J Catal* 2005;236:245–50.