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Reduction of Tb^{4+} ions in luminescent Y_2O_3:Tb nanorods prepared by microwave hydrothermal method

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Abstract: Terbium doped yttrium oxide was prepared with the microwave hydrothermal method. The Y_2O_3:Tb nanomaterial crystallized as needle-like grains. Bright luminescence in the green region was observed. Significant luminescence intensity increase was obtained after thermal treatment. Reduction of terbium ions was observed after heating in the air atmosphere. Tb^{4+} ions were found to be stabilized by crystal impurities. Hydroxyl species were found to have impact on vacancies elimination. The terbium ions were used as optical and magnetic indicator of the material properties.

Keywords: yttrium oxide; terbium; luminescence; biomarkers; abnormal reduction; rare earths

Yttrium oxide has been used in advanced ceramics for the past decades. Recently, new methods of materials fabrication revived the interest concerning doped nanometric yttrium oxide. Y_2O_3 is a wide band gap semiconductor (5.8 eV) of a high dielectric constant κ, which makes it a good host lattice for lanthanide ions. Yttrium oxide also exhibits high chemical and thermal stability as well as bioinertness, permitting its application in biotechnology. Yttrium oxide crystallizes in the cubic system, bixbyite type (space group Ia^3-T_h^7, Z=16). There are 24 C_2 symmetry sites and 8 C_{3i} symmetry sites of cations in the unit cell[1].

Trivalent lanthanide ions exhibit interesting optical properties, as in most cases their emission is due to transitions within the 4f-manifold. The 4f-electrons are well shielded from the environment of the ion which leads to sharp emission lines[2]. Tb^{3+} ion ($4f^8$) exhibits superior luminescence properties and is appreciated for its emission mainly in the green region due to the $^5D_4 \rightarrow {}^7F_J$ transitions. However, terbium also exists as a tetravalent ion, without significant contribution to the emission in the visible region[3]. Previous studies[4] have shown that due to its absorption band in the visible region Tb^{4+} acts as Tb^{3+} luminescence killer. Hence, oxidation of Tb^{3+} ions seems to be one of the main problems in terbium doped luminescent materials.

RE^{3+} doped materials exhibit abnormal reduction behavior, observed first in the Eu doped lattice[5]. The reduction of europium ions was observed after calcination in an oxidative atmosphere although there were few structural or chemical prerequisites for this process to occur[6]. The reduction process is a result of the tendency of lanthanide ions to reach the electronic configuration of a half-filled 4f shell and is also manifested by oxidation of Tb^{3+} ions to attain the +4 valence state. The standard Tb^{4+}/Tb^{3+} reduction potential of +3.1V favors the reduced ion form[7]. The effect of preserving stable electronic configuration is greater in terbium than in europium, with the standard Eu^{3+}/Eu^{2+} reduction potential of –0.35 V. On the other hand, the bixbyite structure allows terbium ions to oxidize easily, due to the presence of oxygen vacancies in the crystal lattice[8]. The relationship between Tb^{3+} and Tb^{4+} in various hosts was discussed in Refs. [4,8,9]. Other studies have shown that filling of the oxygen vacancies with oxygen ions seems to increase the luminescence intensity of Y_2O_3:Tb, independent of the presence of Tb^{4+} ions[10].

As novel methods of nanomaterial synthesis were developed, new material properties were found. Y_2O_3:Tb nanomaterial has been synthesized by the complexation method[11], flame aerosol technology[12], sol-gel process[13,14], combustion process[10,15,16], and others. However, there are very few literature reports concerning Y_2O_3:Tb crystallized by the microwave hydrothermal method. The hydrothermal technology allows fast growth of oxide nanocrystals[17] without the calcination step[18]. High purity of products and narrow distributions of crystallite sizes are obtained, when hydrothermal process is driven

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by microwave radiation[19]. Far from thermodynamic equilibrium crystal growth conditions may result in a material with advantageous properties, which we verified in the present work.

In this paper we discussed the abnormal reduction of terbium ions in microwave-hydrothermally crystallized Y_2O_3 nanocrystals.

1 Experimental

1.1 Synthesis

Yttrium oxide nanopowders were prepared using the hydrothermal technique with microwaves as heating agent. Firstly, the solution of yttrium and terbium ions was prepared by dissolving 13.32 g of yttrium nitrate(V) (99.8%; Aldrich) and 0.08 g of terbium(III) nitrate(V) (99.99%; Aldrich) in distilled water to set the content of terbium to 0.5 mol.%. The clear solution was then alkalized with 25% aqueous ammonia solution (J.T. Baker) to reach pH=10 under stirring. White precipitate appeared and was suction filtered to be separated from mother liquid. To remove the excess of nitrate(V) and ammonium ions, the residue was triply washed with distilled water. Fresh mixture of yttrium and terbium(III) hydroxides was then placed in the 100 mL PTFE vessel of Magnum II reactor (Ertec) and filled with water to 80% of volume. The vessel was then placed in reaction chamber with stainless steel coat. The reaction was performed at the pressure of 6 MPa and temperature *ca*. 280 ºC during 20 min and then the reactor was cooled down to room temperature. The resulting product suspended in water was dried overnight at 40 ºC to obtain white powder. The product was divided into four parts: three calcined at the temperatures of 400, 800, 1200 ºC, and one left uncalcined.

1.2 Analysis

X-ray diffraction measurements were performed using a Phillips X'Pert powder diffractometer working in a Bragg-Brentano geometry. The measurements were conducted in the 2θ range from 20º to 70º with the step of 0.05º and at counting time of 3 s. The Cu Kα radiation (0.154 nm) was used in all the experiments. Samples were prepared by pressing them into steel rings. Processing of raw data was conducted with X'Pert Highscore software. The scanning electron microscopy (SEM) measurements were conducted with a high resolution (1 nm) Hitachi SU-70 microscope, equipped with a characteristic radiation detector (EDX) and cathodoluminescence system GATAN Mono CL3. The photoluminescence (PL) emission and excitation spectra were taken using a Horiba/Jobin-Yvon Fluorolog-3 spectrofluorimeter, equipped with the xenon lamp as an excitation source and a Hamamatsu R928P photomultiplier. The electron paramagnetic resonance (EPR) spectra were taken with a Bruker spectrometer operating at X-band. Thermal analysis was performed using SDT Q600 thermogravimetric analyzer (TA Instruments). Luminescence decays were obtained with 308 nm excitation pulses (time width 20 ns, repetition rate 10 Hz), provided by a Lambda Physik LPX100 excimer laser. Detection path, in right angle in respect to excitation, consisted of a McPherson 0.67 m monochromator, an EMI9659 photomultiplier operating in photon counting mode and a Stanford Research SR430 Multi- Channel Scaler.

2 Results and discussion

2.1 Structure

The X-ray diffraction patterns (XRD) are shown in Fig. 1. The as-grown material is yttrium nitrate(V) hydroxide $Y_4O(OH)_9(NO_3)$ (PDF reference code 79-1352), which crystallizes in the monoclinic system. The presence of both hydroxyl and nitrate(V) groups is related to the chemicals used in the precipitation process. The initial solution contained nitrate(V) ions, which could be trapped during alkalization into the hydroxide structure. These groups were neither removed from the material during washing nor during the microwave hydrothermal process. The presence of the $Y_4O(OH)_9(NO_3)$ phase at applied pressure and temperature conditions is in agreement with previous studies[20]. The mean crystallite size, obtained from the (110) reflex with use of Scherrer's formula, is 38 nm (Fig. 2). However, the size of crystalline domains in the (040) direction is 81 nm, indicating that the crystallites grow nonuniformly in various crystallographic directions. The material calcined at 400 ºC exhibits only a few diffraction reflexes, suggesting short range ordering. Despite broadening of the reflexes, the peaks appear in the positions characteristic for cubic yttria, suggesting phase transformation to this system. The peak broadening corresponds to mean crystallite size be-

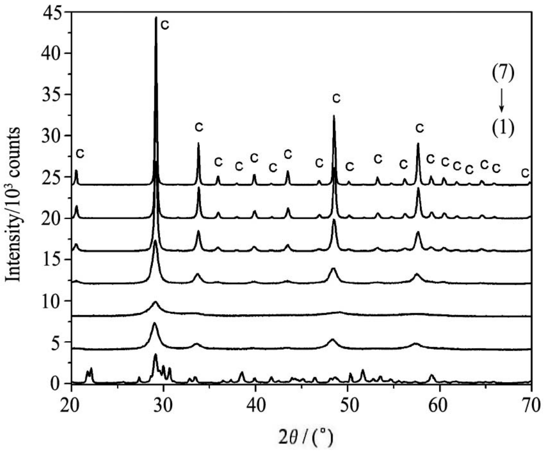

Fig. 1 XRD patterns of Y_2O_3:Tb nanopowders calcined at the different temperatures

(1) As-grown; (2) 200 ºC; (3) 400 ºC; (4) 600 ºC; (5) 800 ºC; (6) 1000 ºC; (7) 1200 ºC