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Original Research Paper

Effect of processing parameters on structural, morphological and optical Y_2O_3:Yb^{3+}/Ho^{3+} powders characteristics

L. Mancic [a,*], V. Lojpur [b], B.A. Marinkovic [c], M.H. de Pinho Mauricio [c], M.D. Dramicanin [b], O. Milosevic [a]

[a] Institute of Technical Sciences of SASA, K. Mihailova 35/IV, Belgrade, Serbia
[b] Vinca Institute of Nuclear Science, University of Belgrade, Belgrade, Serbia
[c] Pontifícia Universidade Católica do Rio de Janeiro – PUC Rio, Departamento de Engenharia de Materiais, Rio de Janeiro, RJ, Brazil

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ABSTRACT

Rod-like and flake-like up-converting Y_2O_3:Yb^{3+}/Ho^{3+} particles which are composed of nanoparticles with size less than 100 nm, are prepared by a simple hydrothermal processing at 473 K (3 h) followed by additional thermal treatment at 1373 K (3 and 12 h). The effect of precursor pH value on the formation of Y_2O_3:Yb^{3+}/Ho^{3+} is followed through X-ray powder diffractometry (XRPD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Structural refinement confirms formation of the cubic bixbyte structure (S.G. *Ia*-3) with the non-uniform accommodation of dopants at C_2 and S_6 cationic sites. Under 978 nm laser excitation, strong green (530–570 nm) up-conversion is observed in all samples. The emission shows a decrease in intensity with an increase in external temperature, indicating FIR (fluorescence intensity ratio) based temperature sensing behavior of 0.52% for the $^5F_4 \rightarrow {}^5I_8/{}^5S_2 \rightarrow {}^5I_8$ transitions.

1. Introduction

Rare earths (RE) doped up-converting phosphors attract a great deal of attention in the photonics industry due to their unique optical properties resulting from electric and magnetic dipole transitions within 4f orbital. Shielded by the outer 5s and 5p shells they exhibit sharp emission lines, at both visible and ultraviolet spectra, suitable for use in laser and display technologies, temperature sensing, bio-labelling and photodynamic therapy. Fine tuning of the resulting emission has been achieved by co- or tri- doping with RE ions that have different electronic structures [1]. During the last ten years, emission of Yb^{3+}/Ho^{3+} co-doped phosphors with different chemical compositions (oxides, fluorides, oxisulphides, etc.) has been reported by many authors [2–6]. Efficiency of the Yb^{3+}/Ho^{3+} couple is based on the fact that Yb^{3+} as a sensitizer with a simply energy level structure could be easily excited by commercial laser diodes (λ = 980 nm) and arouse afterwards Ho^{3+} activator ions *via* energy transfer. Since that Ho^{3+} posses abundant energy levels, after de-excitation to the ground state ultraviolet, visible and (near) infra-red emission could be observed.

There are different mechanisms that govern overall luminescence in up-convertors such as energy transfer up-conversion (ETU), excited state absorption (ESA), addition of photons by energy transfer (APTE) and the photon avalanche (PA). Also, the interaction of dopants with the host matrix is another important factor that affects luminescence [7].

In particular, Y_2O_3 is one of the well known host matrix for RE ions doping owning to its excellent chemical stability and thermal conductivity, broad transparency and low phonon energy. Its cubic crystal structure, space group *Ia*-3, has three times more sites with point-group symmetry C_2 than the sites with point-group symmetry S_6. Since S_6 sites have inversion symmetry electric-dipole transitions are forbidden and therefore the emission originates mainly from dopant ions in the sites with C_2 symmetry. A wide variety of synthesis techniques have been developed for synthesis of Y_2O_3: Yb^{3+}/Ho^{3+} nano- and submicron powders, including wet chemical methods, combustion and laser ablation [8–10]. Particularly, we have also shown that un-agglomerated Y_2O_3:Yb^{3+}/Ho^{3+} spherical submicronic particles with the good chemical homogeneity formed *via* spray pyrolysis process exhibit strong up-conversion, as well as, sufficient temperature sensitivity for thermometry applications at the low temperatures [11].

In the present work, we reported a systematic study of the effects of the precursor pH values, particle shapes and crystallite size on the high temperature up-converting properties of Y_2O_3:Yb^{3+}/Ho^{3+} powders synthesized by a simple hydrothermal method.

* Corresponding author. Tel.: +381 11 2636994; fax: +381 11 2185263.
E-mail address: lidija.mancic@itn.sanu.ac.rs (L. Mancic).

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2. Materials and methods

For the synthesis of $Y_{1.88}Yb_{0.1}Ho_{0.02}O_3$ up-converting powders the low temperature hydrothermal processing is used. The starting reagents are $Y(NO_3)\times 6H_2O$, $Yb(NO_3)\times 5H_2O$, Ho_2O_3, HNO_3 and NH_4HCO_3, all from Sigma Aldrich. More details regarding the synthesis procedure is reported elsewhere [12]. The modification of the previously established synthesis procedure are addressed to composition and adjustment of the precursor pH value either to 7 or 9 through NH_4OH adding prior to the hydrothermal treatment. After hydrothermal processing solid products (denoted as HT7 and HT9) are centrifuged, washed with water up to pH 7 and dried at 373 K for 3 h. The final products are retrieved through additional thermal treatment of as-prepared powders at 1373 K either for 3 or 12 h and are marked as follows: TT7-3h, TT7-12h, TT9-3h and TT9-12h.

The powder's phase composition is determined by X-ray powder diffraction (XRPD) using a Bruker D8 Advance diffractometer with a Cu Kα radiation. The patterns are recorded in the range of 10–80° with a step scan of 0.02 and accounting time of 2 s per step. Analysis the as-acquired XRPD data is done using Le Bail or Rietveld refinement methods in Topas Academic software [13]. FWHM based LVol (volume weighted mean column height) determination of the average crystallite size broadening is modeled by a Voigt function. Peak shapes, lattice parameters and scale are refined simultaneously; after convergence, atomic positions and isotropic temperature factors are included in the refinement. The particles morphology and chemical purity are investigated through secondary emission electron signal on a field-emission scanning electron microscopy (JEOL 6701F) coupled with energy dispersive spectroscopy (JEOL JSM-6510L). Photoluminescence measurements are performed on an Avantes AvaSpec-2048 spectrometer in the temperature interval 273–500 K over 350–900 nm range using 978 nm laser excitation.

3. Results and discussion

The change in precursor pH values prior to hydrothermal processing results in formation of powders with the different phase composition during hydrothermal treatment, Fig. 1. A neutral pH value usually induces crystallization of mixed RE carbonate hydrate as it has been reported previously for the hydrothermally synthesized $(Y_{0.75}Gd_{0.25})_2O_3{:}Eu^{3+}$ powder [14]. Crystallization of this phase is confirmed here as well for the precursor with pH 7. As one could observe from Fig. 1a, $(RE)_2(CO_3)_3(H_2O)_2$ crystallizes in orthorhombic structure, S.G. *Bb*21*m* (ICDD-JCPDS PDF # 81-1538), with the following unit cell parameters (Å): $a = 6.0880(3)$; $b = 9.1581(5)$; $c = 15.1007(8)$. Satisfactory fitting of the HT7 whole powder pattern using Le Bail refinement is achieved after introducing spherical harmonics that describes both peak shapes for anisotropy and intensities for a preferred orientation crystallite growth, suggesting elongated crystallite shape. On the other hand, HT9 sample is composed from monoclinic yttrium hydroxide phase, α-$Y(OH)_3$, S.G. *P*21/*c* (ICDD-JCPDS PDF # 21-1447) with the following unit cell parameters (Å): $a = 6.25(1)$; $b = 6.01(3)$; $c = 15.40$ (2). Alteration of the solid phase composition with the rise of the pH is a consequence of the equilibrium change between precipitated ions and remained ones in the solution during hydrothermal treatment. Increased content of hydroxide anions in solution, owing to NH_4OH addition, prevails over carbonates commencing precipitation of α-$Y(OH)_3$ during hydrothermal treatment. In the majority of the previously published reports related to Y_2O_3 synthesis through hydrothermal treatment of colloids or suspensions obtained through reverse precipitation of starting yttrium salts in alkaline media (NaOH, NH_4OH), formation of hexagonal $Y(OH)_3$ phase (ICDD-JCPDS PDF # 83-2042) is pointed out as the main product. However, a more detail analysis on different compounds stability in the corresponding temperature–pH diagram [15] implicates that hexagonal $Y(OH)_3$ could be generated when pH value is higher than 11.25, while in less alkaline conditions yttrium oxide nitrate hydroxide is the primary phase. In both cases the small quantity of monoclinic α-$Y(OH)_3$ could be also formed at temperatures higher than 473 K. Up to date, formation of monoclinic phase solely under hydrothermal conditions has been reported when yttrium nitrate solution were precipitated with 1 M NH_4OH and treated hydrothermally at 523 K, 60 h [16].

As one could see from Fig. 2(a–b), the morphologies of the hydrothermally synthesized powders are also different. As it is pointed out earlier in the literature [14,15], a correlation among

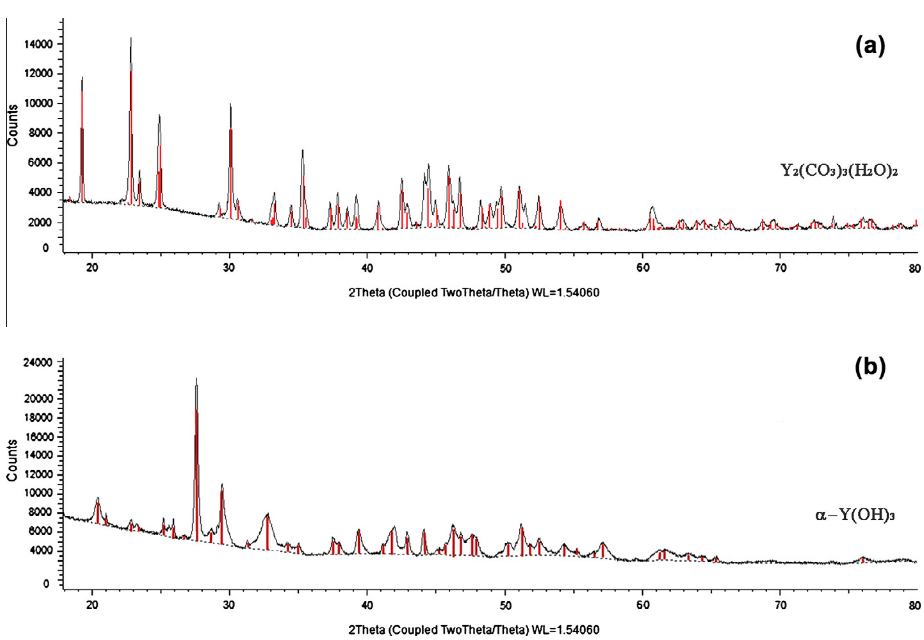

Fig. 1. XRPD patterns of hydrothermally synthesized powders: HT7 (a) and HT9 (b).