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ScienceDirect

Ceramics International 40 (2014) 2915–2926

CERAMICS INTERNATIONAL

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Influence of metal ion concentration in the glycol mediated synthesis of $Gd_2O_3:Eu^{3+}$ nanophosphor

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Received 2 September 2013; received in revised form 30 September 2013; accepted 4 October 2013
Available online 11 October 2013

Abstract

The solvothermal synthesis of highly luminescent and homogeneous $Gd_2O_3:Eu^{3+}$ nanophosphor using diethylene glycol as medium, followed by controlled combustion with citric acid as fuel is reported. The influence of concentrations of carboxylic acid and metal cations on the structure, morphology and luminescence properties are investigated in detail. The microscopic investigations indicate the nanocrystalline nature and the strong influence of cation concentration on the size, shape and agglomeration of the particles. It is found that increase in concentration of metal cations lead to the reduction in agglomeration of nanophosphors. The large value of intensity parameter Ω_2, suggested that Eu^{3+} ions reside in a more asymmetric environment, resulted in intense emission due to $^5D_0$–$^7F_2$ electric dipole transition. Emission decay analysis of the samples exhibited one exponential nature. The samples prepared under optimum conditions showed a quantum efficiency of 78.63% and a moderately high life time of 1.217 ms.

Keywords: A. Powders: chemical preparation; B. Grain size; C. Lifetime; C. Optical properties; Gd_2O_3

1. Introduction

Luminescent nanomaterials with high degree of homogeneity by reliable synthesis routes resulting in defined size, lesser defects and fewer impurities are essential for prospective optoelectronic device applications. Inorganic light emitting materials, namely phosphors have been widely studied by various researchers for applications in high definition television (HDTV), plasma display panels (PDP), cathode ray tube (CRT), flat panel displays (FPD), fluorescent lamps, lighting, medical diagnostics, sensing, defence security ink applications and field emission displays (FED) [1,2]. In the synthesis of phosphors for device applications, the prime areas concerned are morphology, stoichiometry, composition and surface chemistry and for practical applications, high brightness and quantum efficiency are expected [3,4]. In nanophosphors, lattice and surface defects form non-radiative relaxation channels like surface-adsorbed groups resulting in quenching during radiative transition. Interest in rare earth ion doped phosphors is mainly because of their ability to produce visible emission by down and up-conversion processes. Luminescence efficiency of these materials is often limited by the dynamics of the rare earth ions, which depend on the interaction between the rare earth ions and the host, such as local environment around the dopants, concentration of dopants, distribution of activator ions in the host material and the energy transfer from the host to the active ions.

Among rare earth oxides, gadolinium oxide (Gd_2O_3) is a promising host material for both down and up-conversion luminescence applications due to its high density, good chemical durability, thermal stability, photochemical stability and low phonon energy [5–16]. $Gd_2O_3:Eu^{3+}$ is paramagnetic with rich emission properties and is employed in fluorescence lamps, projection television tubes, biological fluorescent labelling, lighting, contrasting agent in magnetic resonance imaging and display applications [1,17–21]. Europium ions can substitute the Gd^{3+} sites in $Gd_2O_3:Eu^{3+}$ and occupy the lattice

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http://dx.doi.org/10.1016/j.ceramint.2013.10.020

sites C_2 and S_6 in cubic phase. Eu^{3+} doped Gd_2O_3 exhibits bright red emission by activating the trivalent rare earth ion Eu^{3+}, through different sensitization processes such as the host Gd_2O_3 absorption, Gd^{3+} ion absorption, Eu–O charge transfer and the Eu^{3+} ion self excitation. For the efficient emission by down conversion, one of the popular ways to sensitize the rare earth emission is through excitation by charge transfer band (CTB). The absorbed energy in CTB is then transferred to the rare earth ions through non-radiative relaxation process.

Usually, luminescent properties like emission lifetime, quantum efficiency and concentration quenching depend on the size and morphology of the phosphor [22,23]. Chemical synthesis routes, like co-precipitation, sol–gel, hydrothermal, combustion methods or synthesis through aerosol offer many advantages over conventional approaches. The precursors are uniformly mixed at the molecular level in a solution based synthesis method giving a high degree of structural homogeneity in the phosphor. Rare earth ion incorporated Gd_2O_3 phosphors have been synthesized in various morphologies like spheres, plates, rods, nanotubes, nanowires, 3D flowers and thin films by a number of techniques such as sol–gel methods, aerosol routes, co-precipitation methods, molten salt routes, chemical vapour deposition, pulsed laser deposition, hydrogen flame pyrolysis methods, non-hydrolytic high temperature methods, combustion methods, spray pyrolysis and hydrothermal routines [5,8,24–33].

Recently, diethylene glycol assisted synthesis of europium incorporated Gd_2O_3 nanophosphor with high degree of homogeneity and enhanced emission was reported [34]. Citric acid has already been employed as shape modifiers to adjust and control the size and morphology of nanoparticles [35,36]. Herein, the dependence of metal cations concentration on the structure, morphology and luminescence of Eu^{3+} doped Gd_2O_3 nanophosphor prepared by solvothermal combustion in diethylene glycol medium is discussed. In this method, citric acid acts as a chelating agent to metal cations via the hydroxyl and carboxyl groups. Judd–Ofelt analysis has been used to obtain the radiative properties of the samples from the emission spectra and dynamic life time measurements.

2. Experimental

Materials used for synthesis were gadolinium oxide (Gd_2O_3, 99.99%, Aldrich), europium oxide (Eu_2O_3, 99.99%, Aldrich), conc. HNO_3 (70%, Merck), polyethylene glycol 200 (PEG, 99%, Merck), diethylene glycol (DEG, $C_4H_{10}O_3$, Merck, 99%) and citric acid monohydrate ($C_6H_8O_7 \cdot H_2O$, A.R. grade). Stoichiometric amounts of Eu_2O_3 and Gd_2O_3 corresponding to the composition $Gd_{1.9}Eu_{0.1}O_3$ were dissolved in concentrated nitric acid and deionized water ($1HNO_3$:$1H_2O$) to prepare their respective nitrate solutions. The solutions were then uniformly mixed by magnetic stirring and citric acid in diethylene glycol was added slowly into the prepared aqueous nitrate solution to chelate metal ions to form metal–citrate complex. The molar concentration ratio of citric acid to metal cations (CM ratio) was varied from 0.5:1 to 3:1 and 2 ml of polyethylene glycol was added to this solution as mineraliser. The mixed solution was then kept at a temperature of about 100 °C with continuous stirring in a water bath until a highly transparent viscous solution is obtained. The resulting viscous solution is then kept at 180 °C for 1 h followed by controlled combustion at 400 °C to obtain greyish precursor. Fully ground precursors were then subjected to sintering at 800 °C for 2 h to obtain the Eu^{3+} doped Gd_2O_3 nanophosphors.

Crystal structure and phase formation of the phosphors were examined using an X-ray diffractometer (Philips PANalytical X'pert Pro) operating at 40 kV and 30 mA with Cu Kα radiation (λ=1.54056 Å) employing X'Celerator and monochromator at the diffracted beam side in the angular range 2θ from 10 to 60°. Phase identification of the samples was performed using the X'Pert Highscore Software along with ICDD-PDF2 database. Low and high resolution transmission electron microscopy (TEM) and selected area electron diffraction (SAED) studies were performed using a FEI Tecnai F20 electron microscope with a field emission gun, operating at 200 KV. The infrared (IR) vibrational spectra of the samples were done in the wavenumber range 400–4000 cm^{-1} by a Fourier Transform Infrared (FTIR) Spectrometer (Shimadzu IRPrestige-21) using the KBr pellet method. The diffuse reflectance (DRS) measurements were carried out on a UV–visible spectrophotometer (JASCO V550) equipped with an integrating sphere (ISV-469) attachment and $BaSO_4$ was used as the reference for measurements to evaluate the band gaps. The Raman spectra of all samples were recorded in backscattering geometry using a confocal micro Raman spectrometer system (Horiba Jobin-Yvon LABRAM-HR800) equipped with a semiconductor diode laser having 785 nm emission (current of 198 mA) and employing a peltier cooled CCD detector. Jobin-Yvon Horiba Fluorolog (FL3-11) Spectrofluorophotometer equipped with a 450 W xenon lamp as the excitation source and a photomultiplier tube in photon counting mode (Hamamatsu R928P) as detector was used to record the excitation and emission spectra at room temperature. The lifetime measurements were recorded using decay by delay method with a FL-1040 phosphorimeter attachment to spectrofluorophotometer employed with microsecond pulsed xenon lamp as the source of excitation. The CIE colour coordinates (x, y) and correlated colour temperature (CCT) of the samples were estimated from the photoluminescent emission spectra based on the 1931 CIE 2 degree colour matching functions. Judd–Ofelt and radiative parameters of the synthesized phosphors were evaluated from the respective emission spectra and dynamic life time measurements.

3. Results and discussion

3.1. Phase analysis, crystal structure and morphology studies

Fig. 1 shows the X-ray diffraction patterns of $Gd_{1.9}Eu_{0.1}O_3$ samples synthesized at 800 °C with different citric acid to metal cation concentration ratios. All the peaks in the diffraction patterns are indexed according to JCPDS file of cubic Gd_2O_3 (JCPDS File no. 12-0797, Ia3 (206) space group, cell