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Energy transfer-based spectral properties of Tb-, Pr-, or Sm-codoped YAG:Ce nanocrystalline phosphors

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Abstract

Tb^{3+}-, Pr^{3+}-, or Sm^{3+}-codoped YAG:Ce nanocrystalline phosphors were prepared using a modified polyol process. Possible tunability of Ce^{3+}-related yellow emission in codoped YAG:Ce nanocrystalline systems was investigated. Dual emission of yellow and red spectral component with a single excitation wavelength was observed from YAG:Ce, Pr or YAG:Ce,Sm codoped systems via an energy transfer from Ce^{3+} and Pr^{3+} or Sm^{3+} ion. It was also observed that the energy transfer event in YAG:Ce, Pr nanocrystalline phosphor occurs mutually between $Ce^{3+} \leftrightarrow Pr^{3+}$, while in YAG:Ce, Sm and YAG:Ce, Tb the energy transfer progresses one way. The detailed pathways for transferring an excitation energy are explained based on the energy level diagrams of respective Ce^{3+}, Pr^{3+}, Sm^{3+}, Tb^{3+} ion.

Keywords: Energy transfer; YAG:Ce; Nanocrystalline; Tunability

1. Introduction

Numerous luminescent nanocrystalline oxides emitting from visible to infrared light can be achieved by introducing transition metal or rare earth elements into oxide hosts [1,2]. Yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$) has been recognized as one of the best phosphor host materials. Various rare earth-doped YAG phosphors are useful in many practical display applications including cathode ray tube, low-voltage field emission display, and backlight source [3–6]. Compared to a conventional high-temperature solid-state reaction synthesis of bulk YAG-based phosphors, nanocrystalline YAG phosphors can be produced by a variety of protocols such as a solvothermal [7–9], co-precipitation [10–12], and combustion method [13].

Cerium-doped YAG (YAG:Ce) is a well-known phosphor which is used as a yellow-emitting component for producing a white light in the liquid crystal display backlight source and the illumination light source. The YAG:Ce with a garnet crystal structure shows a yellow band emission because of the large crystal splitting of ^2D level of Ce^{3+} ion in the garnet structure, resulting in broad excitation and emission bands [3,14].

The tunable yellow emission property of YAG:Ce phosphor may be achieved by the incorporation of an additional codoping element. Few studies on codoped YAG:Ce phosphors have been reported using Pr^{3+} or Tb^{3+} ion [3,4]. Jang et al. [3] reported from Pr^{3+}-codoped YAG:Ce bulk phosphor that the excitation energy of Ce^{3+} ion was transferred to Pr^{3+} ion and a sharp red line peaking at 610 nm through $^1D_2 \rightarrow {}^3H_4$ transition was observed. As another codoped YAG system, i.e., Ce^{3+}-codoped YAG:Tb particle, the efficient energy transfer pathways both from Tb^{3+} to Ce^{3+} ion and from codoped Ce^{3+}-derived YAG lattice defects to Tb^{3+} ion were discussed in terms of cathode- and photo-luminescence, respectively [4].

In this work, Tb^{3+}-, Pr^{3+}-, or Sm^{3+}-codoped YAG:Ce nanocrystalline powders were prepared using a modified polyol protocol, which involves the dissolution of the stabilizer or protecting agent into an aqueous medium and is well suited for the facile, large-scale production of

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nano-sized particles. Our synthetic chemistry can generate a variety of rare earth-doped oxide phosphors or even other types of oxides into a nanocrystalline form. Possible tunability of Ce^{3+}-related yellow emission in codoped YAG:Ce nanocrystalline systems, which are based on one-way or mutual energy transfer between Tb^{3+}, Pr^{3+}, Sm^{3+} versus Ce^{3+} ion, was investigated by systematically varying the concentration of respective codopants.

2. Experimental section

Nano-sized YAG:Ce phosphors were synthesized by a modified polyol process, where polyvinylpyrrolidone (PVP, $M_w = 10{,}000$) is used as a capping agent in the presence of citric acid and water. As-received yttrium, aluminum, cerium, terbium, praseodymium, and samarium nitrates were used without further purification.

In a typical synthesis of standard Ce-doped YAG ($YAG{:}Ce_{0.06}$) nanocrystalline phosphors, 2.260 g of Y nitrate ($Y(NO_3)_3 \cdot 6H_2O$, 99.9%), 3.750 g of Al nitrate ($Al(NO_3)_3 \cdot 9H_2O$, 98 + %), and 0.052 g of Ce nitrate ($Ce(NO_3)_3 \cdot 6H_2O$, 99.999%) were dissolved in 20 mL of water, followed by the addition of 10 g of citric acid and 3 g of PVP into above aqueous mixture. Then the mixture was stirred for 1 h at room temperature. This transparent mixture was placed into a heating mantle and kept at 80 °C with constant stirring for 3 h. Subsequently, the reactants were further heated in the heating mantle at 160 °C for 12 h and became solidified. The as-synthesized products were post-annealed at 1000, 1200, and 1400 °C for 6 h in an air atmosphere. The same protocol was used for synthesis of Tb-, Pr-, or Sm-codoped YAG:Ce nanocrystalline samples, just adding Tb nitrate ($Tb(NO_3)_3 \cdot 5H_2O$, 99.9%), Pr nitrate ($Pr(NO_3)_3 \cdot 6H_2O$, 99.9%), or Sm nitrate ($Sm(NO_3)_3 \cdot 6H_2O$, 99.9%). 0.006–0.1 of Tb, 0.006–0.06 of Pr, or 0.01–0.06 M ratio of Sm was codoped into a standard composition of $YAG{:}Ce_{0.06}$.

Powder X-ray diffraction (XRD) spectra were collected in the step mode, by a Philips APD 3720 X-ray powder diffractometer with Cu Kα radiation. A Hitachi S-4300 scanning electron microscope operated at 10 kV was used to obtain the morphology and size information of YAG nanocrystalline phosphors. Photoluminescence excitation (PLE) and emission spectra of YAG:Ce and codoped YAG:Ce nanocrystalline phosphors were recorded at room temperature by a spectrofluorometer (Fluorolog3, Jobin Yvon Inc.) equipped with a 450 W xenon excitation lamp with a spectral resolution of 1 nm.

3. Results and discussion

General PL characteristics of synthesized $YAG{:}Ce_{0.06}$ nanocrystalline samples are presented in Fig. 1. As shown in Fig. 1(a), Ce^{3+}-related PL emission at 528 nm became stronger with a higher annealing temperature due to an improved crystallinity. Thus, the following samples were post-annealed at 1400 °C for 6 h in air. The Ce^{3+} emission is involved with the ground $4f^1$ and the excited $4f^05d^1$ state. The $4f^1$ and $4f^05d^1$ state are split into $^2F_{7/2}$, $^2F_{5/2}$ and $^2D_{3/2}$, $^2D_{5/2}$ states, respectively, due to the spin–orbital coupling [3,6,15]. The Ce^{3+} emission results from the electron transition from the lowest 5d band to $^2F_{7/2}$, $^2F_{5/2}$ states of the Ce^{3+} ion. Fig. 1(b) shows the typical PLE spectrum of 1400 °C-annealed sample. Two excitation bands are involved with the electronic transitions from the ground state of Ce^{3+} ($^2F_{5/2}$) to the different crystal field splitting bands of excited 5d state of Ce^{3+} ion. The Ce luminescent intensity of nanocrystalline $YAG{:}Ce_{0.06}$ was found to be approximately 60% of that of bulk $YAG{:}Ce_{0.06}$ (which was prepared by a conventional solid state reaction) presumably due to the combined effects of its higher ratio of surface to volume and relatively inferior crystallinity (derived from synthetic nature).

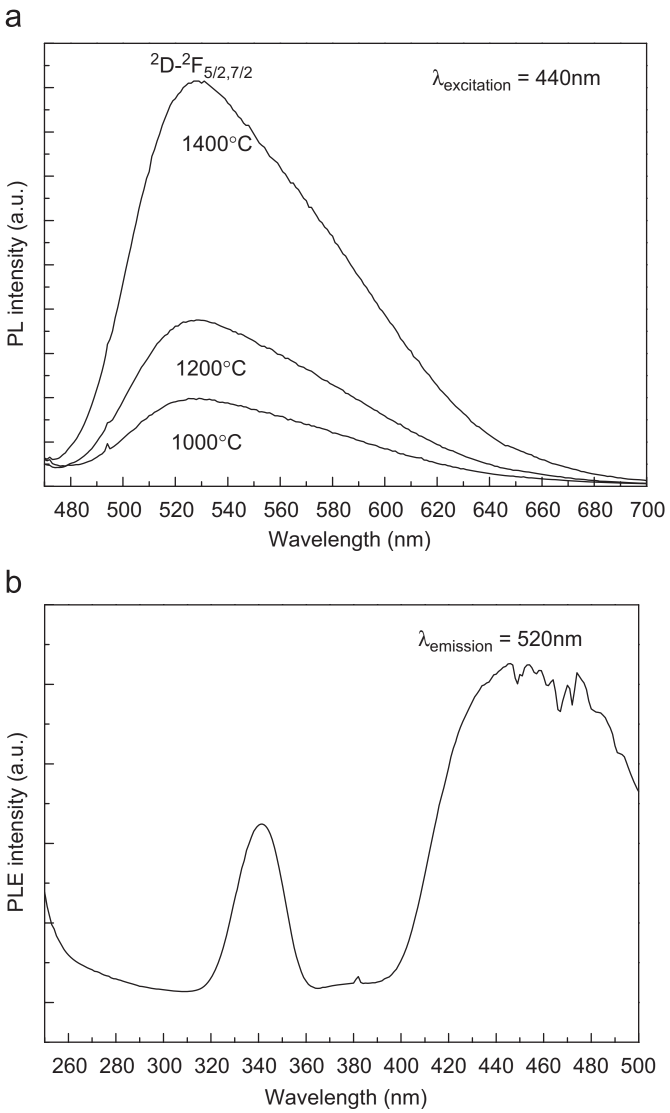

Fig. 1. (a) PL emission spectra of nanocrystalline $YAG{:}Ce_{0.06}$ samples as a function of annealing temperature (excitation wavelength of 440 nm) and (b) PLE spectrum of 1400 °C-annealed sample (detected wavelength of 520 nm).