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Luminescent properties of Gd^{3+} sensitized low-phonon energy $CaGd_4O_7:Tb^{3+}$ green emitting novel phosphors

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Abstract

The trivalent terbium (Tb^{3+}) ions activated $CaGd_4O_7$ (CG) phosphors were synthesized by a sol–gel method. The characterizations were performed after the samples annealed at 1500 °C. The structural and morphological properties were analyzed from the X-ray diffraction patterns and scanning electron microscope images. The photoluminescence excitation spectra showed a broad-band between the wavelengths 250 and 300 nm, which were overlapped with the Gd^{3+} excitation bands. The photoluminescence spectra exhibited efficient green emission due to the sensitization effect of Gd^{3+} ions on the Tb^{3+} ions when exciting with the Gd^{3+} wavelength at 278 nm. In order to analyze the influence of Tb^{3+} concentration on the luminescence behavior of Tb^{3+} ions in the CG host lattice, the decay curves were measured. The temperature-dependent luminescence measurements were done to identify the thermal stability of $CG:Tb^{3+}$ phosphors at elevated temperatures. The cathodoluminescent spectra also showed a similar behavior to that observed in PL spectra. The CIE chromaticity coordinates as a function of Tb^{3+} concentration were calculated and all the obtained chromaticity coordinates have been placed in the green spectral region.

Keywords: A. Sol–gel processes; $CaGd_4O_7$; Luminescence properties; Lifetime analysis

1. Introduction

The trivalent rare-earth (RE^{3+}) ions doped oxide phosphors, which may possibly become promising materials for optoelectronic devices and flat-panel display systems [1–3], have attracted a great attention in order to replace the traditional sulfide phosphors owing to their chemical, mechanical, and thermal stability. It is well known that the RE ions are famous because of their extremely rich $4f^N$ ($N=1$–14, from Ce^{3+} to Yb^{3+}) electronic energy configurations [4]. Several transitions are available between the $4f^N$ states in the visible region, and these transitions are almost insensitive to the local environment because 4f orbitals are shielded by the completely filled 5s and 5p electronic subshells [1,5]. This perception indicates that these active RE ions are not necessarily located in a specific crystal lattice position, as in the case of 4f–5d transitions. However, it is easy to find out the occupation of sites in the host lattice if certain RE^{3+} ions such as (Eu^{3+}, Dy^{3+} and Sm^{3+}) are located in the specified lattice [6,7]. This is an obvious advantage for the development of new types of phosphors, which may decrease the fabrication cost as well. Among these RE^{3+} ions, it is well known that the Tb^{3+} ions emit blue emission at lower concentration and green emission at higher concentration. However, the emission of light not only depending upon the concentration of Tb^{3+} ions but also depending upon the phonon energies of the host lattice [8].

The rapidly expanding market for solid-state lighting creates a need for the development of novel phosphors with high conversion efficiencies, excellent thermal quenching behavior and the efficient emissions in the visible spectral range. Unlike incandescent and fluorescent lamps, LEDs are not characteristically white light sources. LEDs emit light in a very narrow range of wavelengths in the visible spectrum, resulting in nearly monochromatic light. Thus, LEDs are so efficient for colored light applications

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such as traffic lights and exit signs. At present, mainly two ways to make White light-emitting diodes (WLEDs) i.e., blue LED chip coated with yellow phosphor and the tri-band (Red, Green, and Blue) based WLEDs, which have been fabricated by pumping the UV-A (320–400 nm) LED sources. The tri-band based WLEDs offer good color flexibility both in multicolor displays and different shades of white and also excellent color rendering index [9].

Generally, phosphors are prepared by a traditional solid-state reaction method [10]. This approach naturally requires high temperature, time-consuming heating process and subsequent grinding [3,7,11–13]. The grinding process damages the phosphor surfaces, causing the loss of emission intensity. Additionally, phosphor particles prepared through this solid-state reaction method are large in size (generally in micrometer range). However, in recent years, several wet chemical techniques such as the co-precipitation method [14], combustion [15], hydrothermal [6], solvothermal [2], spray-pyrolysis [16], and sol–gel [17] were employed to prepare the phosphor precursor. Among these techniques, the sol–gel process has attracted much attention because of its advantages for obtaining the novel chemical compositions with unique properties, excellent purity and relatively low reaction temperature resulting in more homogeneous products, and it is also possible to synthesize phosphors with small sizes [18].

To the best of our knowledge, so far no reports have been found on the luminescent properties of $CaGd_4O_7$ (CG) host lattice based phosphors. In this work, we reported on the synthesis of Tb^{3+} activated monoclinic CG host lattice by means of a sol–gel process, together with the detailed analysis of X-ray diffraction (XRD) patterns, scanning electron microscope (SEM), photoluminescence (PL) along with decay curves, temperature-dependent luminescence and cathodoluminescence (CL) properties.

2. Experimental

The $CaGd_4O_7$ nanocrystalline phosphors with different concentrations of Tb^{3+} were prepared by means of the sol–gel method by taking the stoichiometric amounts of high-purity grade calcium nitrate hexahydrate $[Ca(NO_3)_2 \cdot 4H_2O]$, gadolinium nitrate hexahydrate $[Gd(NO_3)_3 \cdot 6H_2O]$, terbium nitrate pentahydrate $[Tb(NO_3)_3 \cdot 5H_2O]$ and citric acid $[HOC(COOH)(CH_2COOH)_2]$. One solution was prepared by dissolving the 1 mM of calcium nitrate, 2 mM of citric acid in de-ionized (DI) water. The other solution was prepared by dissolving the $4(1-x)$ mM of gadolinium nitrate, $4x$ mM of terbium nitrate and 8 mM of citric acid in DI water. The two solutions were stirred individually by the magnetic stirrer for 30 min, and then they were mixed and stirred until a homogeneous solution was formed. The mixture was then heated on a hot plate with continued magnetic stirring, and the solution temperature was maintained at 80 °C. Firstly, the beaker was closed with a cap for 12 h and then the cap was removed. After opening the cap, the solution was evaporated within 1 h and yellowish wet gel was produced. The gel was dried at 120 °C, which yields porous solid matrices called xerogel. The drying was accompanied by liquid expulsion from the pores (syneresis) and substantial matrix shrinkage often leads to cracks (mainly due to the capillary pressure). This precursor decomposed to give black-colored flakes with extremely fine particle size by further calcination at 400 °C for 4 h. The resulting sample was further annealed at 1500 °C for 10 h. But Tb doped phosphors showed no emission after annealing treatment in the ambient atmosphere, which indicates that all the Tb ions are in the tetravalent state. To convert Tb^{4+} to Tb^{3+} for obtaining emission properties, all the heat treatment powders were then fired under a reduced atmosphere (4% H_2/96% Ar) at 1400 °C for 3 h, and the powders body color changes from yellow to white. This indicates that all terbium ions are in the trivalent state.

3. Results and discussion

Fig. 1 shows the XRD pattern of $CaGd_4O_7$ (CG) powder phosphor sample, which was annealed at 1500 °C for 10 h. At this temperature the CG phosphor was well crystallized into monoclinic phase with the space group B2/m. The calculated lattice constants are $a=22.43$, $b=8.81$, and $c=3.73$, which were very close to the standard JCPDS card [PDF (72-2492)]. Typically, the crystallite size can be estimated by using the Scherrer equation, $D_{hkl}=k\lambda/(\beta \cos\theta)$, where D is the average grain size, k (0.9) is a shape factor, λ is the X-ray wavelength (1.5406 Å), β is the full width at half maximum (FWHM) and θ is the diffraction angle of an observed peak. The strongest diffraction peaks are used to calculate the crystallite size, which yield an average value of about 98.4 nm. The inset of Fig. 1 shows the SEM image of the CG:Eu^{3+} phosphors annealed at 1500 °C. The closely

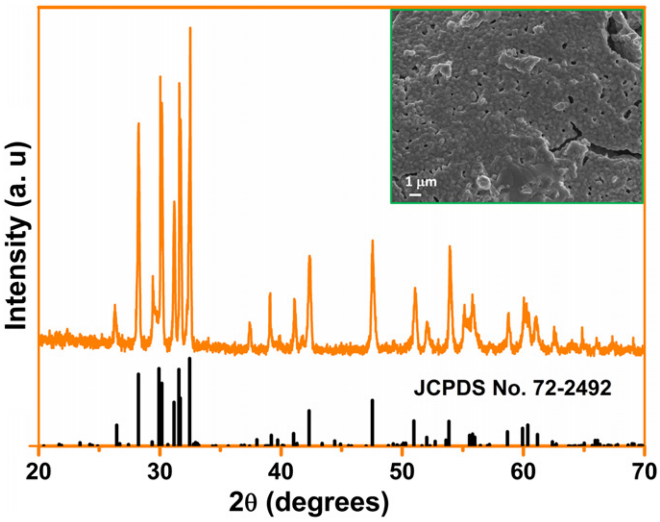

Fig. 1. XRD pattern of CG:2 mol% Tb^{3+} phosphor and the inset shows the corresponding SEM image.