Facile combustion synthesis of novel $\text{CaZrO}_3\text{:Eu}^{3+}$, Gd^{3+} red phosphor and remarkably enhanced photoluminescence by Gd^{3+} doping

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Abstract. A facile sol–gel combustion route was reported for the direct preparation of $\text{CaZrO}_3\text{:Eu}^{3+}$ and $\text{CaZrO}_3\text{:Eu}^{3+}$, Gd^{3+} . The obtained deposits were characterized by XRD, TGA-DSC, SEM, EDS, PL measurements and microscope fluorescence. When the Gd^{3+} ions were introduced in this compound, the emissions of $\text{CaZrO}_3\text{:Eu}^{3+}$ were remarkably enhanced. The emission spectrum of $\text{CaZrO}_3\text{:Eu}^{3+}$, Gd^{3+} nanocrystals exhibited a red shift compared with $\text{CaZrO}_3\text{:Eu}^{3+}$ samples. A new mechanism of the improved photoluminescent properties of Eu^{3+} by Gd^{3+} was investigated. The optimized phosphor $\text{CaZrO}_3\text{:5%Eu}^{3+}$, 2%Gd^{3+} could be considered an efficient red-emitting component for white lighting devices excited in the near-ultraviolet region.

Keywords. Photoluminescence; $\text{CaZrO}_3\text{:Eu}^{3+}$, Gd^{3+} ; sol–gel combustion; optical property.

1. Introduction

Luminescence materials play an important role in display applications. Oxide phosphor nanocrystals have been extensively investigated in fundamental and technological research. With the development of new types of high-efficiency and high-resolution displays, there is an increasing demand for high-quality phosphors with sufficient brightness and long-term stability.^{1–3} Because of high melting point and stable physical and chemical properties, perovskite-type oxide phosphors can steadily work in various environments. CaO-ZrO_2 system has attracted much attention of material scientists. However, most of these investigations are focussed on the preparation and characterization of CaO stabilized ZrO_2 . Little research work has been carried out on CaZrO_3 , especially on the preparation and luminescence properties of nanosized CaZrO_3 .^{4,5} In addition, CaZrO_3 was traditionally synthesized by solid-state reaction, which needs high temperature to obtain pure CaZrO_3 . Compared with the conventional method, sol–gel combustion method has advantages for preparing ultrafine materials due to its low cost, high yield and controlled reaction process.^{6–8}

The enhancement of the luminescent efficiency is a very important issue in phosphor materials. It has been proved that a doped nanostructure may suppress resonant energy transfer and therefore leads to high-quality phosphor. Trivalent Eu ions have been utilized in many oxides as doping ions.

Numerous luminescence investigations have been focussed on the Eu^{3+} ions. The activator Eu^{3+} ions are located at low symmetric sites, and the excitation probabilities of Eu^{3+} f-f transitions in the near-ultraviolet (NUV) region become strong. Photoluminescence (PL) from Eu^{3+} -doped host is characterized by a series of sharp emission bands located in red spectral region, which can be assigned to the electronic transitions $^5\text{D}_0\text{--}^7\text{F}_j$ ($j = 0, 1, 2, 3, 4$).^{9–11} In the literature, Eu^{3+} is used to produce the red emission. The energy transfer of Gd^{3+} to Eu^{3+} exists in many luminescent processes of various phosphors, such as $(\text{Y}, \text{Gd})\text{BO}_3\text{:Eu}^{3+}$, Gd^{3+} ;¹² $\text{LaPO}_4\text{:Eu}^{3+}$, Gd^{3+} ;¹³ $\text{RbGd}_3\text{F}_{10}\text{:Eu}^{3+}$, Gd^{3+} ;¹⁴ $\text{GdF}_3\text{:Eu}^{3+}$, Gd^{3+} ;¹⁵ and $\text{K}_5\text{Li}_2\text{GdF}_{10}\text{:Eu}^{3+}$, Gd^{3+} .¹⁶ However, to the best of our knowledge, there is no report on the study of the preparation and PL properties of nanosized $\text{CaZrO}_3\text{:Eu}^{3+}$, Gd^{3+} . Additionally, we investigated a new mechanism for the improved PL properties of Eu^{3+} by Gd^{3+} in our work, which is different from the traditional energy transfer mechanism.

Oxide phosphors (in particular, red phosphors) with excitation spectra matching the NUV excitation are rare. Therefore, there is an urgent need to produce red-emitting phosphors, which can be efficiently excited by NUV light.^{17,18} In this paper, we report a fast and efficient procedure for obtaining pure, Eu^{3+} doped and Eu^{3+} , Gd^{3+} co-doped CaZrO_3 nanoparticles, which does not require any annealing step. The phase structure and morphology were characterized by X-ray diffraction (XRD) and scanning electron microscope (SEM). Especially, the PL properties were investigated after the doping of $\text{Eu}^{3+}/\text{Gd}^{3+}$ ions.

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2. Experimental

2.1 Sample preparation

The phosphors $\text{CaZrO}_3:\text{Eu}^{3+}$ and $\text{CaZrO}_3:\text{Eu}^{3+}, \text{Gd}^{3+}$ were prepared by the sol-gel combustion method at a relatively low temperature. Starting chemicals used in this study were as follows: calcium nitrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), zirconyl acetate ($\text{ZrO}(\text{AC})_2$) with 20.05 wt% ZrO_2 , citric acid, ammonium nitrate (NH_4NO_3), europium oxide (Eu_2O_3), gadolinium oxide (Gd_2O_3) and nitric acid. All the reagents were analytically pure and used without further purification.

In a typical synthesis, 2.5 mmol $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was dissolved in 20 ml deionized water and 1.19 ml $\text{ZrO}(\text{AC})_2$ was added into this aqueous solution under stirring. Then 10 mmol ammonium nitrate was added in the resultant solutions. After even mixing, 3.12 ml citric acid solution (1 mol l^{-1}) was injected into the solution fast to get white sol. The molar ratio of metal ions to ammonium nitrate and citric acid were 1:4 and 1:1.25. The whole process was always under magnetic stirring at room temperature. The resultant sol was heated in a drying oven at 100°C for 2 days to prepare the xerogel. Then the products were removed into crucibles and introduced into a muffle furnace maintained at 700°C for 30 min, cooling to room temperature naturally.

$\text{Eu}(\text{NO}_3)_3$ (0.05 mol l^{-1}) and $\text{Gd}(\text{NO}_3)_3$ (0.05 mol l^{-1}) were gained by dissolving Eu_2O_3 and Gd_2O_3 into diluted HNO_3 . The Eu^{3+} doped and $\text{Eu}^{3+}, \text{Gd}^{3+}$ co-doped CaZrO_3 nanophosphors were synthesized just as mentioned above, except that $\text{Eu}(\text{NO}_3)_3$ and $\text{Gd}(\text{NO}_3)_3$ were introduced.

2.2 Characterization

The phase purity of the prepared phosphors was checked by powder XRD patterns (type Germany Bruker axs D8-Advance X-ray diffractometer with graphite monochromatized Cu K irradiation ($\lambda = 1.542 \text{ \AA}$)). Data were collected over the 2 theta range of 20° – 70° , with a step width of 0.02° and count time of 0.2 s per step. After the powder was dried at 100°C for 2 days, thermogravimetric analysis and differential scanning calorimeter were carried out simultaneously on the same portion of sample on SDT Q600 TGA-DSC equipment. The analyses were carried out in air, at a heating rate of $10^\circ\text{C min}^{-1}$ from room temperature up to 800°C . The morphology was characterized with SEM (type JEOL JSM-6700f). The composition measurement was operated by energy dispersive spectrometric (EDS) analysis (Horba EMAX Energy, EX-350). The excitation and emission spectra of all the samples were recorded using an Edinburgh FLS920. The luminescence observation of the samples was measured by the fluorescence microscope (type Olympus IX81). All the measurements were performed at room temperature.

3. Results and discussion

3.1 Structural and morphology

The XRD patterns of pure CaZrO_3 , $\text{CaZrO}_3:\text{Eu}^{3+}$ and $\text{CaZrO}_3:\text{Eu}^{3+}, \text{Gd}^{3+}$ are shown in figure 1. One of the advantages of sol-gel combustion method is the low temperature and heating at 700°C for 30 min leads to the formation of well-crystallized CaZrO_3 . In comparison, much higher temperature (more than 1400°C) is needed for the preparation of well-crystalline CaZrO_3 by conventional heating. The main diffraction peaks in figure 1 indexed well with the structure of CaZrO_3 according to JCPDS 35-0645 data file. Faint impurity peaks (marked with rhombus) may be caused by ZrO_2 or precursors that do not react completely during the combustion process due to the fact that the combustion wave is not uniform.^{19,20} And minor impurities such as ZrO_2 are hardly avoided at such a low calcination temperature and such a short time.²¹ Figure 1 also indicates that the small amount of doped rare earth of Eu^{3+} and Gd^{3+} ions did not cause significant change in the host structure and the phase composition of phosphors in our experimental range.

Figure 2 shows the TGA-DSC curves of the precursor gel of pure CaZrO_3 dried at 100°C for 2 days. The TGA curve displays three main weight loss stages. The first weight loss is approximately 54.84% below 258°C , accompanied by two endothermic peaks around 126 and 241°C and one exothermic peak around 202°C in the DSC curve, which are caused by the evaporation of water and the organic components such as acetic acid and the combustion of organic components such as citric acid, respectively. The other two stages of weight loss at temperatures between 258 and 600°C are primarily due to the further combustion of the remaining organic groups and the citrate, accompanied by two big

Figure 1. XRD patterns of pure, 5% Eu^{3+} and 5% Eu^{3+} , 2% Gd^{3+} -doped CaZrO_3 samples obtained at 700°C .

Figure 2. TGA–DSC curves of pure CaZrO_3 precursor gel powder.

Figure 3. SEM micrographs of (a) pure CaZrO_3 , (b) CaZrO_3 : 5% Eu^{3+} , 2% Gd^{3+} and (c) EDS spectra of the CaZrO_3 :5% Eu^{3+} , 2% Gd^{3+} samples.

exothermic DSC peak in the range of 280–500°C with 12.84 and 13.48% weight loss, respectively. After the combustion process reaches an end, the sample undergoes no more transformations.

The morphology of the crystallites was inspected using SEM. Figure 3a and b shows the microstructures of pure CaZrO_3 and CaZrO_3 : Eu^{3+} , Gd^{3+} , respectively, which show that the grain size is below 100 nm. It reveals that the samples show a strong tendency to form agglomerates, as shown in figure 3. We see no obvious impact on the morphology or particle size as the dopant ions are introduced. Especially, the chemical composition of the CaZrO_3 :5 mol% Eu^{3+} , 2 mol% Gd^{3+} sample was inspected by using the EDS. The EDS spectrum shows the europium and gadolinium signals besides the Ca, Zr and O signals. The actual Eu^{3+} and Gd^{3+} concentration estimated by figure 3c are 4.3 and 1.2 mol%, clearly indicating the presence of appropriate Eu^{3+} and Gd^{3+} ions incorporated into the phosphors.

3.2 Photoluminescence properties

PL excitation and emission spectra of Eu^{3+} -doped CaZrO_3 measured at room temperature are shown in figures 4 and 5, respectively. Some excitation peaks centered at 363 nm ($^7\text{F}_0/5\text{D}_4$), 384 nm ($^7\text{F}_0/5\text{G}_2$), 395 nm ($^7\text{F}_0/5\text{L}_6$), 466 nm ($^7\text{F}_0/5\text{D}_2$) and 536 nm ($^7\text{F}_1/5\text{D}_1$) can be seen in figure 4.^{22–24} Generally, the excitation spectrum changes with the variation of the crystal field strength in the bond length, symmetry and covalence because of the different doping ions. However, the excitation spectrum in our work hardly varies except for the intensity with Gd^{3+} dopant. It is possibly due to the similar radius of the dopant ions: Eu^{3+} : 0.95 Å and Gd^{3+} : 0.938 Å. Thus, the excitation spectra of CaZrO_3 : Eu^{3+} , Gd^{3+} is not seen. To understand the red phosphor

Figure 4. Excitation spectra of Eu^{3+} -doped CaZrO_3 sample ($\lambda_{\text{em}} = 614 \text{ nm}$).

Figure 5. Emission spectra of $\text{CaZrO}_3:\text{Eu}^{3+}$ samples with varied Eu^{3+} doping concentration. The inset shows the evolution of the emission intensities centered at 614 nm with varying of Eu^{3+} concentrations ($\lambda_{\text{ex}} = 395$ nm).

application for white-light devices, the dominant ${}^7\text{F}_0/{}^5\text{L}_6$ transition with maximum at 395 nm was employed as excitation wavelength for acquiring the Eu^{3+} emissions.

In order to investigate the effect of the dopant concentration on PL intensities, the concentrations of Eu^{3+} dopants were varied. The experiments showed that the concentration of the dopants had little effect on the wavelength position of emission peaks, but the PL intensity changed considerably by varying Eu^{3+} content. Figure 5 shows two main emission peaks appeared at about 591 and 614 nm under an excitation of 395 nm. The most intense peak at 614 nm corresponds to the ${}^5\text{D}_0/{}^7\text{F}_2$ transition within Eu^{3+} ions, while the peaks at 591 nm correspond to ${}^5\text{D}_0/{}^7\text{F}_1$. It can be seen that doping Eu^{3+} ions into CaZrO_3 changes the intensity of emission bands in figure 5. With the increasing of the Eu^{3+} concentration, intensity of emission band around 614 nm increases and reaches a maximum at Eu^{3+} concentration of 5 mol%. A further increase of the Eu^{3+} content leads to decreased luminescent intensities due to concentration quenching, a phenomenon arising from enhanced probability of energy transfer among the Eu^{3+} activators themselves due to the shortened distance among adjacent Eu^{3+} ions.^{25,26} The optimum value is almost 5.2 times that of $\text{CaZrO}_3:0.5\% \text{Eu}^{3+}$, which can be seen clearly from the inset of figure 5. The main emission peaks of Eu^{3+} , which are ${}^5\text{D}_0/{}^7\text{F}_1$ (591 nm) and ${}^5\text{D}_0/{}^7\text{F}_2$ (614 nm), have different transition probabilities as one is primarily a magnetic dipole transition (${}^5\text{D}_0/{}^7\text{F}_1$) and the other is primarily an electric dipole transition (${}^5\text{D}_0/{}^7\text{F}_2$). The forced electric dipole (ED) transition ${}^5\text{D}_0/{}^7\text{F}_2$ is hypersensitive to local environment, while the magnetic dipole (MD) transition ${}^5\text{D}_0/{}^7\text{F}_1$ is insensitive to the site symmetry. Thus, the MD/ED emission ratio can be used as a measurement of the site symmetry of Eu^{3+} .^{27,28} It is clearly shown from figure 5 that the emission

Figure 6. Excitation and emission spectra of $\text{CaZrO}_3: 2\%\text{Gd}^{3+}$ sample.

peak centered at 614 nm is much more intense than that of 591 nm, indicating that the ED transition is dominant and Eu^{3+} ions prefer to hold a low symmetry site without an inversion centre.

Figure 6 presents excitation and emission spectra associated with Gd^{3+} ions in CaZrO_3 . The sharp peaks are assigned to the typical 4f/4f intraconfiguration forbidden transitions of Gd^{3+} . The major emission peak of Gd^{3+} was at 315 nm, which corresponds to the transition ${}^6\text{P}_1/{}^8\text{S}_{7/2}$. This luminescence can be excited at the ${}^6\text{I}_1$ (276 nm) levels. Keeping Eu^{3+} at the optimal content of 5 mol%, we investigated the effects of Gd^{3+} addition on the PL properties of the red phosphors (figure 7). Because the f-f transition absorption bands of Gd^{3+} ions are mainly distributed in the 240–320 nm, the transition of Gd^{3+} from the ground ${}^8\text{S}_{7/2}$ state to various higher excited states are not accessible under 395 nm excitation. Thus, little of energy transfer occurs from Gd^{3+} to Eu^{3+} ions. Gd^{3+} is assumed to replace the site of Eu^{3+} due to the same valence and similar ion radius (Eu^{3+} (0.95 Å) and Gd^{3+} (0.938 Å)). The substitution of Eu^{3+} by Gd^{3+} increases the average distance of $\text{Eu}^{3+}\text{--Eu}^{3+}$, reducing the energy nonradiative transition caused by the cross-relaxation between the emission ions. Therefore, the emission intensity of $\text{CaZrO}_3:\text{Eu}^{3+}$ is remarkably enhanced by incorporation of Gd^{3+} ions.^{29,30} The emission intensities reach the peak maximum at a co-dopant concentration of 2 mol% Gd^{3+} and decrease after that. On the other hand, the substitution of Eu^{3+} by Gd^{3+} in CaZrO_3 samples decreases the symmetry of Eu^{3+} site in CaZrO_3 lattice. The ratio of ED to MD enhanced obviously from 1.42 to 1.76 with the increasing Gd^{3+} -doping concentration from 0 to 2%, as calculated according to figure 7. Hence, it confirms Eu^{3+} substituted with Gd^{3+} ions in CaZrO_3 increases the disorder of ligand field and decreases the centrosymmetric nature of Eu^{3+} site in CaZrO_3 sample. Experiments show that the 614 nm luminescent intensity of the phosphor $\text{CaZrO}_3:5\% \text{Eu}^{3+}, 2\%$

Figure 7. Emission spectra of $\text{CaZrO}_3\text{:Eu}^{3+}$, Gd^{3+} samples with varied Gd^{3+} doping concentration. The inset shows the evolution of the emission intensities centered at 614 nm with varying of Gd^{3+} concentration ($\lambda_{\text{ex}} = 395$ nm).

Figure 8. CIE chromaticity diagram for $\text{CaZrO}_3\text{:Eu}$, Gd . The inset shows the microscope fluorescence image of $\text{CaZrO}_3\text{:5% Eu}^{3+}$, 2% Gd^{3+} sample.

Gd^{3+} is roughly 3.1 times that of the $\text{CaZrO}_3\text{:5% Eu}^{3+}$ one. Additionally, the emission peak arising from $^5\text{D}_0/7\text{F}_2$ transition of $\text{CaZrO}_3\text{:5% Eu}^{3+}$, $x\% \text{Gd}^{3+}$ show a red shift with the increasing content of Gd^{3+} ion doping, as shown in figure 7. When x changed from 0 to 0.02, the emission peak value increased from 610.6 to 614.6 nm, which had a red shift of 4 nm. The red shift in PL spectra could be attributed to the

strengthening of the crystal field and smaller lattice dimensions due to Gd^{3+} substitution for Eu^{3+} . Thus, with increasing concentration of Gd^{3+} , the energy corresponding to the transition from lower ^5D component to the ^7F state of Eu^{3+} is thus expected to become smaller, leading to a red shift in the emission spectrum.³¹ It suggests that the incorporation of Gd^{3+} could enhance the red component of white LED.

The chromaticity coordinates of the phosphors were calculated based on their PL spectra, and are shown in the CIE chromaticity diagram (figure 8). The CIE chromaticity coordinates of the $\text{CaZrO}_3\text{:5 mol% Eu}$, 2 mol% Gd sample is (0.627, 0.371). The microscope fluorescence image in the inset of figure 7 indicates that the $\text{CaZrO}_3\text{:5% Eu}^{3+}$, 2% Gd^{3+} phosphor could be used as red components for white lighting devices excited in the NUV region. Because of the even light and strong brightness, the phosphors could have potential applications.

4. Conclusion

In summary, phosphors $\text{CaZrO}_3\text{:Eu}^{3+}$ and $\text{CaZrO}_3\text{:Eu}^{3+}$, Gd^{3+} were synthesized by a simplified sol-gel combustion approach and the reaction temperature was decreased in a large scale in comparison with the conventional solid-state method. Their PL properties were investigated in this work. The most intense excitation peak centered at 395 nm ($^7\text{F}_0/5\text{L}_6$). The emission spectra consist of two strong peaks at about 591 and 614 nm, corresponding to the MD transition $^5\text{D}_0/7\text{F}_1$ and the forced ED transition $^5\text{D}_0/7\text{F}_2$. When the Gd^{3+} ions are introduced into this compound, the average distance $\text{Eu}^{3+}\text{--Eu}^{3+}$ is increased, reducing the energy nonradiative transition caused by the cross-relaxation between the Eu^{3+} ions. Therefore, the emissions of Eu^{3+} are enhanced until the doping concentration reaches 2 mol%. The microscope fluorescence image indicates that the phosphor $\text{CaZrO}_3\text{:5% Eu}^{3+}$, 2% Gd^{3+} could find a potential application on the NUV white LED.

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