

Eu, Dy codoped $Y_2Zr_2O_7$ powders with white light luminescence

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ABSTRACT

Eu, Dy codoped $Y_2Zr_2O_7$ crystalline powders have been prepared by a simple sol-gel-combustion method. The luminescence excitation and emission spectra of the products were measured, and the CIE chromaticity was introduced to characterize the color of the phosphor. It was found that the emission color of the Eu, Dy codoped $Y_2Zr_2O_7$ powders depends on the doping concentration of Eu, Dy ions and the excitation wavelength. White light emission has been observed for $Y_2Zr_2O_7: 1.5\%Eu^{3+}, 2.0\%Dy^{3+}$ under 350nm excitation, for which the calculated chromaticity coordinate is (0.37, 0.32). Copyright © 2011 VBRI press.

Keywords: Luminescence; phosphor; white light; rare earth.



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Introduction

Plenty of efforts have been made to the fabrication of effective white light emitting phosphors [1-10], driven by the development of white light-emitting diodes (LEDs), which have been considered as a potential replacement for the conventional illumination devices in the viewpoints of low electric consumption, high brightness, long lifetime and environment friendly characters. Rare earth (RE) ions doped metal oxide crystalline powders are potential phosphors with several advantages such as chemical stability, heat-resistance and long working life. However, one type of RE ion in a matrix usually shows a special luminescence emission which can only cover a small range of the visible light spectrum. To obtain full color emission and even the white light emitting, one feasible route is the codoping of various RE ions.

Both Eu^{3+} and Dy^{3+} are well known as activator dopants for many different inorganic lattices. Phosphors doped with Eu^{3+} usually emit red or orange red light [11-13], due to the intraconfigurational $f-f$ transitions [14] of Eu^{3+} , from the excited 5D_0 state to 7F_J ($J = 1, 2, 3, 4, 5$) levels of $4f^6$. The $4f$ energy levels of Eu^{3+} are hardly affected by the crystal field because of the shielding effect of the $5s^25p^6$ electrons. The luminescence of Dy^{3+} mainly focuses on the blue and green range, with two emission peaks at 480nm and 575nm, corresponding to ${}^4F_{9/2} - {}^6H_{15/2}$ and ${}^4F_{9/2} - {}^6H_{13/2}$ transitions respectively. It can be supposed that the white light emission can be achieved with appropriate combination of the red emitting Eu ions and blue/green emitting Dy ions. In fact, europium and dysprosium ions co-doped zinc-aluminoborosilicate glasses have been prepared and a white light emission was obtained [1].

Crystalline powders are good host materials for luminescent rare earth ions, for their better heat-resistance and luminescence variety than glasses. We have reported an effective red emitting phosphor based on crystalline yttrium zirconate ($Y_2Zr_2O_7$) [15]. It has been confirmed that $Y_2Zr_2O_7$ is a good base material. In the present work, Eu, Dy codoped $Y_2Zr_2O_7$ crystalline powders were researched, expecting a white light emission. The luminescence spectra were analyzed in detail and the chrominance was discussed.

Experimental

Eu^{3+} , Dy^{3+} codoped $Y_2Zr_2O_7$ ($Y_2Zr_2O_7: Eu^{3+}, Dy^{3+}$) luminescent powders have been synthesized by a simple sol-gel-combustion method [15]. Typically, $Y(NO_3)_3$ (partially replaced by $Eu(NO_3)_3$ and $Y(NO_3)_3$ according to the doping concentration), $ZrO(Ac)_2$ and NH_4NO_3 were first mixed in the molar ratio of 1:1:3. After 30min stirring, the requisite amount of urea was added to the mixed solution. The mixture was stirred for 1h, and then the transparent sol was heated to give an opal gel. Ammonia solution was needed to adjust pH value of the solution to be 7~8. The as-prepared gel was dried at 100°C for 12h, and then heated in a muffle furnace at 600 °C for 10 min. The phase composition was identified by using X-ray diffraction (XRD, D8-Advance, and Bruker, Germany). The microstructures images were taken using a scanning electron microscope (SEM, S-2500, and Hitachi, Japan). The photoluminescence (PL) spectra were measured with an Edinburgh FLS920 fluorescence spectrometer at room temperature. The spectral resolution is 1.0 nm.

Results and discussion

All the samples were named by the molar ratio of doping ions to Y^{3+} ions (For example, $Y_2Zr_2O_7: 1.5\%Eu^{3+}, 1.0\%Dy^{3+}$ means that 1 molar of $Y_2Zr_2O_7$ doping with 3% molar of Eu^{3+} and 2% of Dy^{3+}).

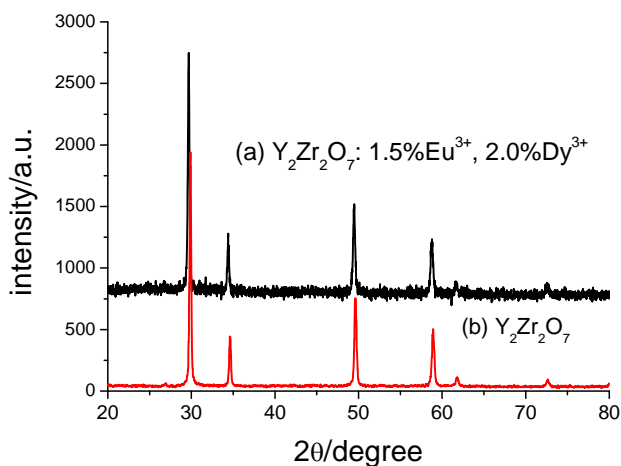


Fig. 1. XRD patterns of (a) $Y_2Zr_2O_7: 1.5\%Eu^{3+}, 2.0\%Dy^{3+}$, and (b) $Y_2Zr_2O_7$.

Fig. 1 shows the XRD patterns of Eu^{3+} , Dy^{3+} codoped and pure yttrium zirconate. All the four main peaks (2 2 2), (4 0 0), (4 4 0) and (6 2 2) are in agreement with the formation of fluorite structured $Y_2Zr_2O_7$ [11]. From **Fig. 1**, no impurity phase such as the Eu_2O_3 and Dy_2O_3 was detected in the doped sample. A small shift of the diffraction peaks is attributed to the lattice distortion resulted from the accommodation of Eu^{3+} and Dy^{3+} in the $Y_2Zr_2O_7$ lattice.

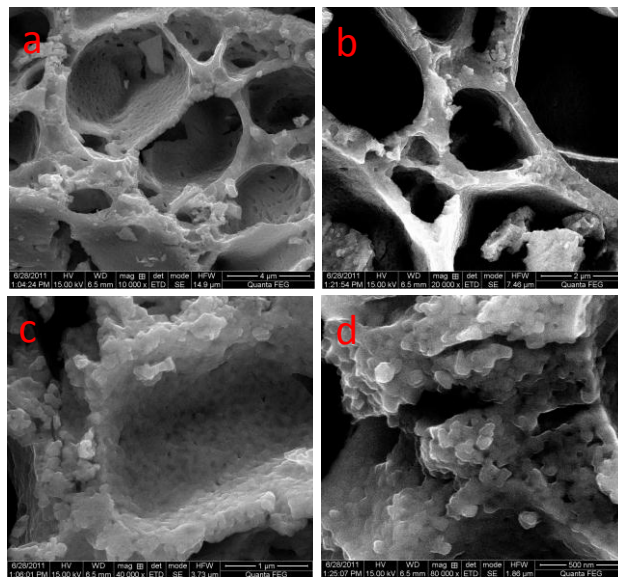


Fig. 2. SEM pictures of $Y_2Zr_2O_7: 1.5\%Eu^{3+}, 2.0\%Dy^{3+}$ at (a) 10 kX, (b) 20 kX, (c) 40 kX and (d) 80 kX.

The typical SEM images are shown in **Fig. 2**. The sample showed multipore structure consisting of small particles. The size of the particle is about 100nm. **Fig. 3** shows the luminescence emission spectra of Eu^{3+} doped and Eu^{3+} , Dy^{3+} codoped $Y_2Zr_2O_7$ powders. $Y_2Zr_2O_7: 1.5\%Eu^{3+}$ powders show typical emission of Eu^{3+} (as shown in Fig. 3 (a)) The emission peak around 590 nm is assigned to ${}^5D_0 - {}^7F_1$ transition, the peaks at 610nm and 630nm are assigned to ${}^5D_0 - {}^7F_2$, the peak around 650nm is assigned to ${}^5D_0 - {}^7F_3$, and the peak around 710nm is assigned to ${}^5D_0 - {}^7F_4$ transition. For $Y_2Zr_2O_7: 1.5\%Eu^{3+}, 1.0\%Dy^{3+}$, an additional peak appeared around 485nm, and the peak at 590nm was widened that results from the existing of another peak around 583nm. The enhancement of luminescence at 485nm and 583nm are ascribed to the ${}^4F_{9/2} - {}^6H_{15/2}$ and ${}^4F_{9/2} - {}^6H_{13/2}$ transitions of Dy^{3+} respectively. The relative emission intensity between Dy^{3+} and Eu^{3+} varied as the excitation wavelength, resulting in different spectra shapes. The relative intensity of Dy^{3+} is lowest when the excitation wavelength is 239nm, and is highest when the excitation wavelength is 350nm. The excitation of 239nm is attributed to the charge transfer state (CTS) of Eu^{3+} , which is caused by the electron transferred from the oxygen 2p orbital to the empty 4f orbital of europium [16-18]. Thus light at 239nm can only excite Eu^{3+} ions in the $Y_2Zr_2O_7$ host. As a result, characteristic Eu^{3+} emission was observed under 239nm excitation.

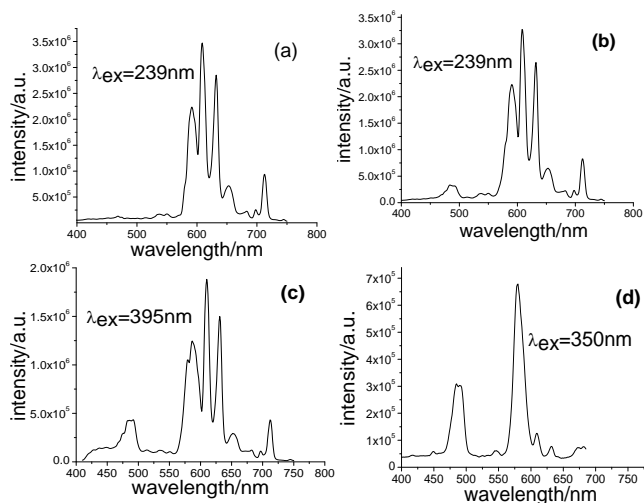


Fig. 3. Emission spectra: (a) $\text{Y}_2\text{Zr}_2\text{O}_7: 1.5\% \text{Eu}^{3+}$, excited at 239nm, (b), (c) and (d) $\text{Y}_2\text{Zr}_2\text{O}_7: 1.5\% \text{Eu}^{3+}, 2.0\% \text{Dy}^{3+}$. (b) is excited at 239nm, (c) at 395nm, and (d) at 350nm.

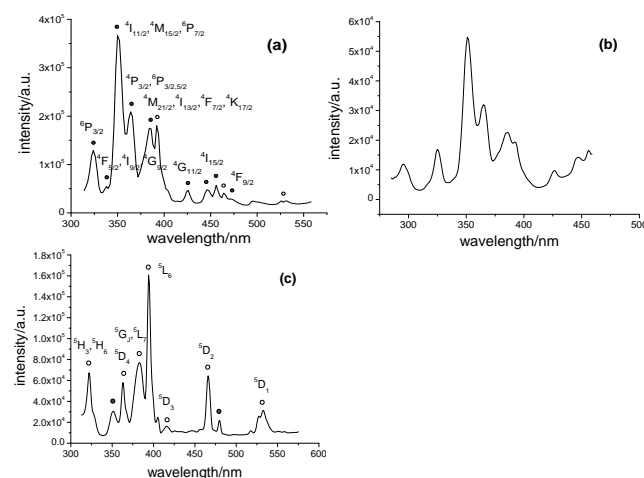


Fig. 4. Excitation spectra of $\text{Y}_2\text{Zr}_2\text{O}_7: 1.5\% \text{Eu}^{3+}, 1.0\% \text{Dy}^{3+}$ with the emission wavelength monitored at (a) 583nm, (b) 485nm, and (c) 610nm. (Solid circles indicate the transitions of Dy^{3+} , hollow circles indicate the transitions of Eu^{3+}).

Fig. 4 (a)-(c) shows the excitation spectra of $\text{Y}_2\text{Zr}_2\text{O}_7: 1.5\% \text{Eu}^{3+}, 1.0\% \text{Dy}^{3+}$ powders as the emission wavelength was monitored at 583nm, 485nm and 610nm respectively. Most of the excitation peaks in **Fig. 4 (a)** and **(b)** are attributed to transitions from the ${}^6\text{H}_{15/2}$ ground state to various excited states of Dy^{3+} , and there are also several weak peaks attributed to transitions of Eu^{3+} (as shown in **Fig. 4 (a)**). It can also be found that the relative intensity of Eu related excitation peaks are even weaker for 485nm emission. The excitation peaks for 610nm emission are mainly attributed to the transitions from the ${}^7\text{F}_{0,1}$ ground state to various excited states of Eu^{3+} as shown in **Fig. 4(c)**. It can be inferred from the excitation spectra that the luminescence emission around 485nm is primarily originated from the Dy^{3+} , the emission around 610nm is from Eu^{3+} , and the emission around 583nm both from Dy^{3+} and Eu^{3+} . That is to say, the relative emission intensity in different wavelength ranges can be adjusted by switching the exciting light wavelength.

Therefore, the emission light color of the Eu, Dy codoped $\text{Y}_2\text{Zr}_2\text{O}_7$ can be monitored through controlling the doping ratio of Eu and Dy ions or controlling the wavelength of excitation light. **Fig. 5** shows the emission spectra of $\text{Y}_2\text{Zr}_2\text{O}_7: 1.5\% \text{Eu}^{3+}, 2.0\% \text{Dy}^{3+}$ under excitation of different wavelength. The relative intensity of emission in the blue and green range and in the red range varies as the excitation wavelength. Except the characteristic emissions of Dy^{3+} and Eu^{3+} , a broad emission band has also been observed around 440nm, which is ascribed to the 5d-4f transition of Eu^{2+} . This result indicates that the doped Eu^{3+} ions can be partly reduced to Eu^{2+} ions during the fabrication of the material.

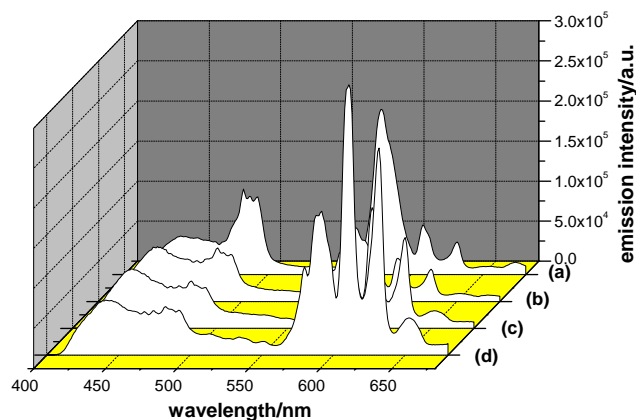


Fig. 5. The emission spectra of $\text{Y}_2\text{Zr}_2\text{O}_7: 1.5\% \text{Eu}^{3+}, 2.0\% \text{Dy}^{3+}$ powders excited at (a) 350nm, (b) 366nm, (c) 380nm, (d) 395nm.

The excitation and emission spectra for the different combinations have been given in **Fig. 6**. It is found that no obvious energy transfer occurs for the samples with low doping concentration, but for $\text{Y}_2\text{Zr}_2\text{O}_7: 10\% \text{Eu}^{3+}, 2.0\% \text{Dy}^{3+}$, the energy transfer does occur.

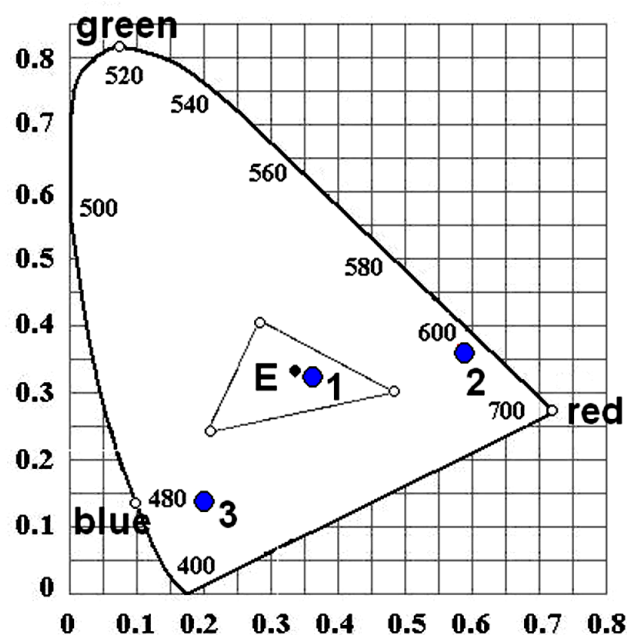


Fig. 6. CIE chromaticity diagram for emission of $\text{Y}_2\text{Zr}_2\text{O}_7: 1.5\% \text{Eu}^{3+}, 2.0\% \text{Dy}^{3+}$ under 350nm excitation (1), $\text{Y}_2\text{Zr}_2\text{O}_7$ under 239nm excitation (2), and $\text{Y}_2\text{Zr}_2\text{O}_7: 10\% \text{Eu}^{3+}, 2.0\% \text{Dy}^{3+}$ under 366nm excitation (3).

Table 1. CIE chromaticity coordinates of luminescence emission of $Y_2Zr_2O_7$ with different Eu and Dy concentration under 350nm excitation.

Sample	Eu concentration (%)	Dy concentration (%)	x (red)	y (green)
1	1.5	0	0.58	0.36
2	1.5	1.0	0.41	0.39
3	1.5	1.5	0.43	0.38
4	1.5	2.0	0.37	0.32
5	1.5	2.5	0.37	0.33
6	3.0	2.0	0.33	0.26
7	5.0	2.0	0.42	0.34
8	10	2.0	0.31	0.20

Table 1 shows the CIE chromaticity coordinates (value of x and y) calculated from the emission spectra of Eu, Dy codoped $Y_2Zr_2O_7$ with different doping concentration. The standard white light corresponds to the situation that both the value of x and y is equal to 0.33. It is found from Table 1 that most of the samples are apt to red emission, and Sample 4 is the one that is closest to white light emission. Fig. 6 is the chromaticity diagram for the emission of three typical samples, $Y_2Zr_2O_7$: 1.5% Eu^{3+} , 2.0%Dy $^{3+}$, pure $Y_2Zr_2O_7$, and $Y_2Zr_2O_7$: 10% Eu^{3+} , 2.0%Dy $^{3+}$. The chromaticity coordinate of $Y_2Zr_2O_7$: 1.5% Eu^{3+} , 2.0%Dy $^{3+}$ under 350nm excitation lies in the white light area in the diagram. The coordinates of pure $Y_2Zr_2O_7$ under 239nm excitation and of $Y_2Zr_2O_7$: 10% Eu^{3+} , 2.0%Dy $^{3+}$ under 366nm excitation are near to pure red and pure blue respectively. It was thus proved that various color emission can be obtained by controlling the Eu, Dy codoping concentration and excitation wavelength. Especially white light emission was achieved in $Y_2Zr_2O_7$: 1.5% Eu^{3+} , 2.0%Dy $^{3+}$ at 350nm excitation.

Conclusion

A new phosphor Eu, Dy codoped $Y_2Zr_2O_7$ has been introduced. The emission color of the phosphor was found adjustable by controlling the doping concentration of Eu, Dy ions and the applied excitation wavelength. The CIE chromaticity results indicate the color of the Eu, Dy codoped $Y_2Zr_2O_7$ ranged from red to blue. The calculated chromaticity coordinate is (0.37, 0.32,) for $Y_2Zr_2O_7$ powder doped with 1.5% Eu^{3+} and 2.0%Dy $^{3+}$ and under 350nm excitation, which lies in the white light area.

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