Advances in Intelligent Systems Research, volume 168

International Conference on Modeling, Analysis, Simulation Technologies and Applications (MASTA 2019)

Luminescence Property of Eu^{3+}-doped $CaZrSi_2O_7$ Phosphors for White LEDs

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Keywords: LED, Phosphor, Synthesis, Luminescent properties.

Abstract. Eu^{3+}-doped $CaZrSi_2O_7$ phosphors with promising luminescent properties have been successfully prepared through microwave heating. The crystallinity and luminescent performance were characterized by powder X-ray diffraction pattern, photoluminescence spectra, respectively.

The results show that the obtained Eu^{3+}-doped $CaZrSi_2O_7$ phosphors have good crystallinity, and strong emission under near-ultraviolet (NUV) light excitation, which emits red colors peaking at 615 nm, corresponding to the $^5D_0 \rightarrow {}^7F_2$ electric-dipole transition of Eu^{3+} which shows the rare earth Eu^{3+} ions are located in noncentrosymmetric sites.

The red emission of Eu^{3+}-doped $CaZrSi_2O_7$ phosphors is excellently consistent with CIE chromaticity standards. It is suggested that the as-prepared Eu^{3+}-doped $CaZrSi_2O_7$ samples have high potential for phosphor-converted white LEDs application.

Introduction

In recent years ,white light emitting diodes (W-LEDs) which are regarded as a new solid state light soures have been widely used in many fields such as displays and lighting because of its many merits of high compact size, low energy consumption, higher luminous efficiency, environmental friendliness and longer lifetime[1,2].

Although the efficiency of commercially white LEDs which were usually prepared through combining blue LED chip with yellow $Y_3Al_5O_{12}:Ce^{3+}$ phosphors is high, the color rending index is relatively low due to a lack of sufficient red component[3].

To overcome these problems, phosphor-converted white LEDs have been paid special attention to as it provides high CRI. The availabile commercially phosphors for near UV excited LEDs are mostly red $Y_2O_2S:Eu^{3+}$, green $ZnS:Cu^+,Al^{3+}$ and blue $BaMgAl_{10}O_7:Eu^{2+}$. However, $Y_2O_2S:Eu^{3+}$ and $ZnS:Cu^+,Al^{3+}$ phosphors were instability (releasing of sulfide gas) under UV irradiation and result in low quantum efficiency. In the case, recently a lot of researchers have made extensive efforts to search for new phosphor for white LEDs aplication and through effectively combining red, green and blue emitting phosphors togather to enhance color rending index [4-6].

Nowadays,silicates have attracted much attention to be applied to luminescent materials due to its advantages of outstanding chemical stability and optical performance[7,8]. Moreover, rare earth ion doped silicates phosphors have been widely investigated due to its excellent application in white light emitting diodes [9-11].

Furthmore, a lot of advantages have been found through microwave-induced method to prepared solid oxide materials compared to the conventional synthesis mehtod in terms of its heating mode [12-13], which microwave can heat the material at the molecular level, so that the heating is uniform. In addition, in the preparing process by microwave-induced method, the reaction time is not long and it is not needed to apply expensive instrument, which makes the technology attractive.

In the work, by using improving microwave heating prepare process, a pure phase Eu^{3+}-doped $CaZrSi_2O_7$ (abbrev:CZSO) phosphor for white light emitting diodes application have been successfully prepared. Moreover, The microstructures and luminescent perpormance of the prepareded samples were analyzed in detail.

Experimental

The raw materials were Silicon dioxide (analytical pure), Calcium oxide (analytical pure), Zirconium dioxide (analytical pure) and Europium oxide (9.999%). A stoichiometric amount of metal oxides were weighed on the basis of stoichiometric ratio of $Ca_{1-x}ZrSi_2O_7$:xEu. The weighed mixed powder was grounded evenly in an agate mortar for 50 minutes, subsequently the mixed powder was placed into alumina crucible. Finally, the crucible containing mixture powders were put into a HAMiLab-C1500 microwave furance (1500 W, 2450 M Hertz,600-1500℃). The fired temperature were set at 1100℃. After 5 h of irradiation, the sample was cooled to room temperature in the oven, and then ground, pulverized for subsequent analysis.

The crystallinity of the prepared samples synthesised in the microwave-induced method was analyzed by X-ray powder diffraction. The morphologies were investigated by Field emission electron microscopy. The spectral distribution was characterized by spectrofluorometer.

Results and Discussions

The XRD pattern of the $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} sample prepared by the microwave synthesis process was showen at Figure 1. The results show that the X-ray diffraction pattern is in good agreement with the pattern of $CaZrSi_2O_7$ in the monoclinic system registered by JCPDS (No.33-0322). The diffraction lines are well assigned to $CaZrSi_2O_7$ crystalline phase and correspond to the space group C2/m, which indicates that Eu^{3+} (ionic radius 0.95 Å) replaced Ca^{2+} (ionic radius 0.99 Å). Moreover, no uncorrelated diffraction peaks are shown in the X-ray diffraction pattern. Therefore, the XRD result shows the phosphor obtained by improving microwave heating synthesis process is monophasic.

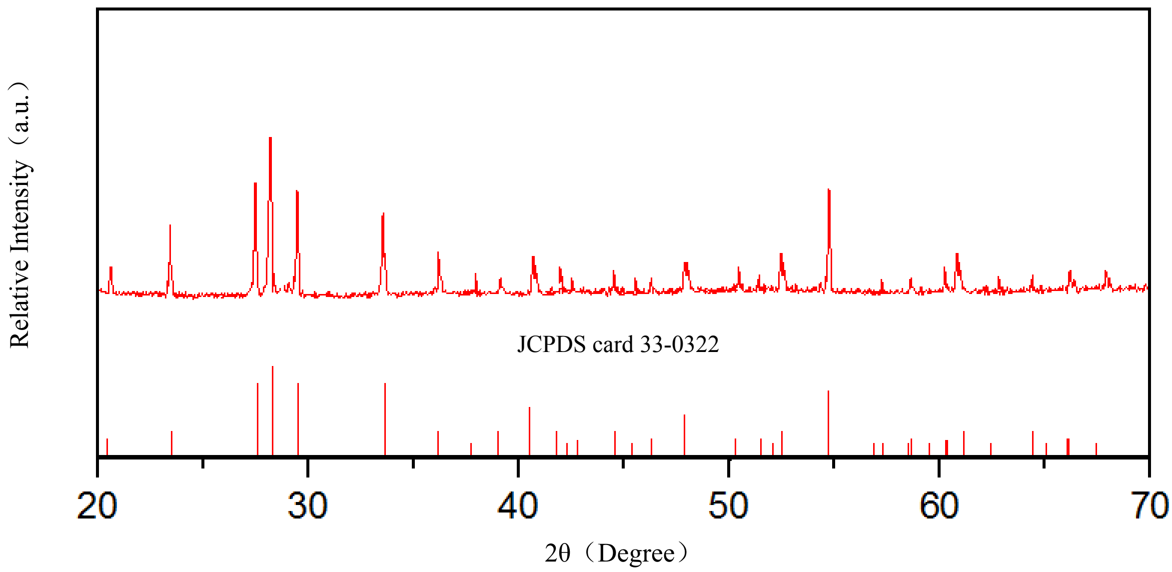

Figure 1. XRD pattern of the $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} sample

The luminescence characteristics of obtained $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} （CZSO）phosphors were prominent and the excitation spectrum of the prepared samples was shown in Figure 2. As shown at the Figure 2, the excitation spectra of the CZSO samples showed a series of sharp lines at 350nm-500nm, which derived the excitation bands of Eu^{3+} luminescence centers corresponding to the characteristic transition of the Eu^{3+} ion. They are ascribed to the $^7F_0$–$^5D_4$, $^7F_0$–$^5G_2$, $^7F_0$—$^5L_6$, $^7F_0$—$^5D^3$ and $^7F_0$—$^5D_2$ transitions at 362 nm, 380 nm, 394 nm, 412 and 465 nm of the Eu^{3+} ion, respectively[14]. Therefore, the results indicates that dopant Eu^{3+} ions has been introduced into $CaZrSi_2O_7$ lattices as the Eu^{3+} to replace Ca^{2+} sites because the ionic radius of Ca^{2+} is similar to that of

Eu^{3+} (Ca^{2+} is 0.99 Å, Eu^{3+} is 0.95 Å). The Eu^{3+} excitation band made it well matched with the emission spectra of UV white light emitting diodes.

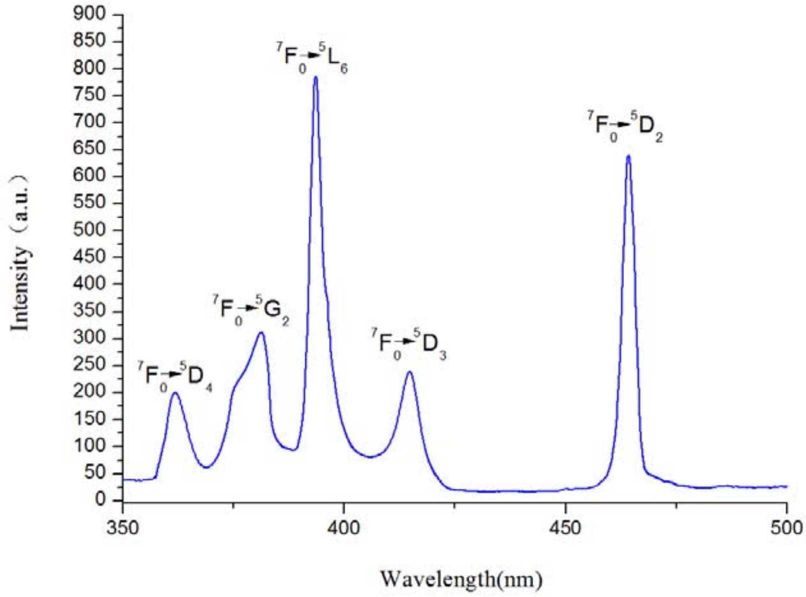

Figure 2. Excitation spectra of $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} (CZSO) phosphor

The emission spectra excited by 394 nm of the obtained $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} phosphors have been showen at Figure 3. The 394 nm excitation produced several strong emission peaks with the peaks at 578, 589, 615, 655, and 702 nm, respectively, which they are ascribed to the $^5D_0$–$^7F_0$, $^5D_0$–$^7F_1$, $^5D_0$–$^7F_2$, $^5D_0$–$^7F_3$ and $^5D_0$–$^7F_4$ transitions[15]. The predominant emission peak is at 615nm, corresponding to the $^5D_0 \rightarrow ^7F_2$ electric-dipole transition of Eu^{3+} which shows the rare earth Eu^{3+} ions are located in noncentrosymmetric sites. The energy level diagram for Eu^{3+} ion has been shown in Figure 4.

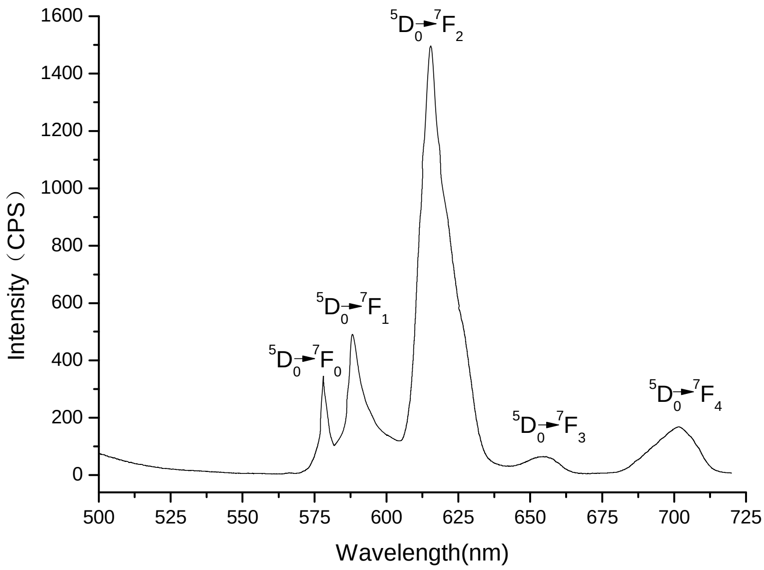

Figure 3. Emission spectra of $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} phosphor

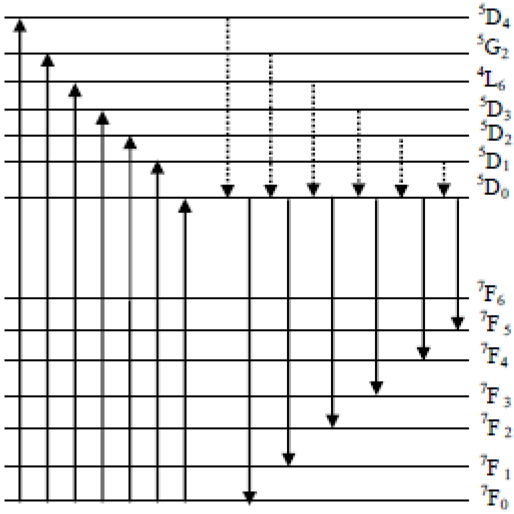

Figure 4. Energy level diagram for Eu^{3+}

The emission spectra of the prepared $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} phosphors has been at Figure 5. For comparison, conventional solid method was employed to prepare $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} samples. It can been seen from the Figure 5 that the fluorescent powder synthesized by improved microwave heating method has higher emission intensity than that synthesized by traditional solid method. The microwave heating materials is fundamentally different from that of traditional methods [16]. Microwave internal heat and volume heat cause many hot spots, which make the phosphor easy to crystallize completely, thus reducing the number of defects in the phosphor , so that the prepared phosphor has higher luminous capacity.

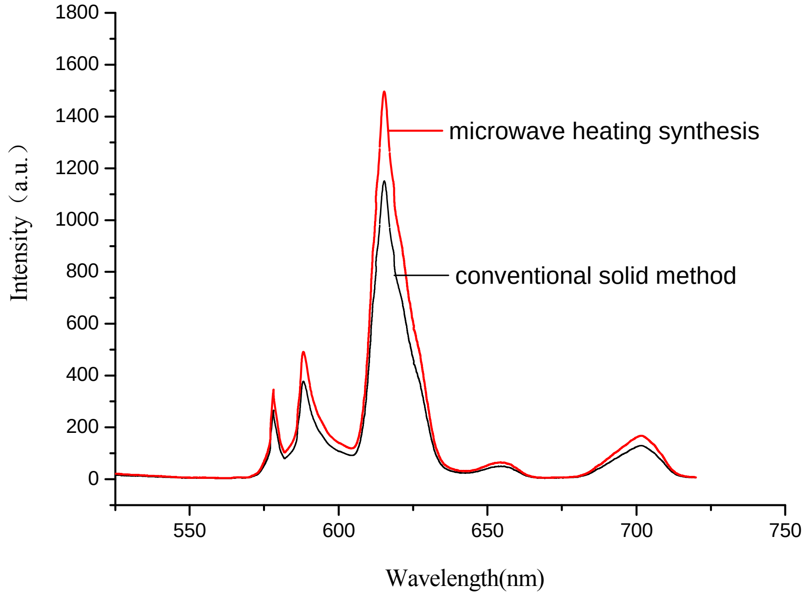

Figure 5. Comparison of emission spectra of $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} obtained from microwave heating synthesis and conventional solid method

Conclusion

$Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} phosphor has been successfully synthesized through an improving microwave heating method. The measured result by XRD indicated a well-crystallized, monophasic $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} crystallite. The prepared $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} phosphors exhibited a excellent luminous performance. The Eu^{3+} excitation spectra show the obtained samples being well-matched with the emission of UV light emitting diodes. Moreover, the resultant $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} phosphors exhibited a higher luminous capacity compared to ones prepared by traditional solid process. It is suggested that the as-prepared $Ca_{0.9}ZrSi_2O_7$:0.1Eu^{3+} products have high potential for the application by phosphor-converted white LEDs.

Acknowledgment

The work was supported by Technology Plan of Department of Education of Jiangxi (No.Gjj151139),China. A lot of thanks to Jiangxi Science and Technology Support Plan （No.20171BAB206040) and Program of Jiangxi Province Key Laboratory of Precision Drive and Control（No.PLPDC-KFKT-201614）. In addition, authors would grateful to the Innovative Foundation Project for Under-graduates.

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