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Photoluminescence of Red-Emitting Phosphor Sr2CeO4: Eu3+, Sm3+ for Light-Emitting Diodes

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Abstract. The red-emitting phosphor Sr2CeO4: Eu3+, Sm3+ was synthesized by conventional high-temperature solid-state method. X-ray diffraction, and photoluminescence spectra were used to characterize the as-synthesized phosphor. In Eu3+ singly doped Sr2CeO4 phosphors, Eu3+ ion showed a weaker 7F0–5L6 transition at 395 nm with a narrow line and could not be efficiently excited by the NUV–LED chip. In Sm3+, Eu3+ co-doped Sr2CeO4 phosphors, the energy transfer from Sm3+ to Eu3+ in Sr2CeO4 host is observed and investigated in detail. The absorption band around 404nm was broadened and the intensities of the main emission line (5D0→7F2 transition of Eu3+ at 614nm) were strengthened because the energy transfer from Sm3+ to Eu3+. Moreover, The chromaticity coordinates of Sr2CeO4: Sm3+ can be regulated to approach the NTSC standard values of red phosphor by codoping Eu3+ ions. The photoluminescence properties suggest that novel Sr2CeO4: Eu3+, Sm3+ phosphor might have a potential research value on white-LEDs.

Introduction

In recent years, White light-emitting diodes (W-LEDs) have been called as the new generation of solid state lighting source with its long lifetime, low energy consumption, Small volume, high luminescence efficiency and environmental-friendly characteristics[1,2]. The most general strategy of producing white light is to employ the yellow phosphor YAG:Ce^{3+} with the blue LED chips [3]. However, due to the lack of a sufficient red emission component in the visible spectrum, this combination leads to low color-rendering index (CRI) and high correlated color temperature (CCT), which limited their potential applications [4]. With the development of chip technology , alternatively, another the commonly method is coating the near ultraviolet (NUV) LED or UV-LED chips with the primary tricolor (RGB) multi-phased phosphors [5]. Unfortunately, some problems also appear. Such a multi-phosphors combination, leading to decreased luminous efficiency due to reabsorption of different emission colors [6]. Moreover, the efficiency of Y_2O_2S:Eu^{3+} red phosphor among the tricolor multi-phased phosphors is much lower than that of the green and blue phosphors. In addition, the lifetime of the Y_2O_2S:Eu^{3+} is inadequate under NUV irradiation for its instability [7,8]. Consequently, it is urgent to search for novel and highly efficient red phosphors that can be excited by NUV (350 -420 nm).

A suitable red-emitting NUV-LED phosphor should meet the following necessary conditions in general: the host is stable, the phosphor exhibits strong and broad absorption around ~400 nm , which matches well with the radiation of NUV-LED chip, and the phosphor shows high efficiency under NUV excitation and with the chromaticity coordinates near the NTSC (National Television Standard Committee) Standard values.

In order to search for red-emitting phosphors with high efficiency and proper CIE chromaticity coordinates, the Eu^{3+}-activated phosphors are primarily considered. The trivalent europium ion is well-known as a red-emitting activator due to its particular spectral character [9-11]. In the past work, We have already reported Eu^{3+} ion doped Sr_2CeO_4 due to their absorption band around 395 nm, which matches with the radiation of NUV–LED chip [12]. However, in Sr_2CeO_4:Eu^{3+} system, Eu^{3+} ion showed a weaker $^7F_0$–$^5L_6$ transition at 395 nm with a narrow line and could not be efficiently excited by the NUV–LED chip. In order to strengthen and broaden the absorption around ~ 400 nm, one of the effective method is introduced a co-doped ions as an activator in the phosphors. The Sm^{3+} ion has been widely used as an activator of reddish orange emission and its efficient absorption band of NUV is at around 405 nm, which is in good agreement with the absorption peak ($^6H_{5/2}\rightarrow{}^4K_{11/2}$) of Sm^{3+}. Hence, Sm^{3+} ions are expected to be ideal activator for red phosphor for NUV-LEDs. Accordingly, In Sm^{3+}, Eu^{3+} co-doped phosphors system, through the energy transfer from Sm^{3+} to Eu^{3+} maybe enhance the absorption band around ~ 400 nm, which have been confirmed in molybdate system [13, 14].

Therefore, In this paper, we synthesized Sm^{3+} and Eu^{3+} co-doped Sr_2CeO_4 phosphors and investigated the co-doped effects of Sm^{3+} ions on the luminescence properties for Sr_2CeO_4:Eu^{3+} phosphor and found that Sr_2CeO_4 :Sm^{3+}, Eu^{3+} phosphor might be a potential red phosphor for NUV-LEDs.

Experimental

A series of $Sr_{2-x-y}CeTi_xO_4$: xEu^{3+}, ySm^{3+} phosphor samples with different concentrations of Eu^{3+} and Sm^{3+} were synthesized by a high temperature solid-state method. The starting materials $SrCO_3$ (99%), CeO_2 (99.99%), TiO_2 (99%), Sm_2O_3 (99.99%) and Eu_2O_3 (99.99%) were weighed according to appropriate stoichiometric ratio and ground evenly in agate mortar. A proper amount of H_3BO_3 (99.5%) was added to serve as flux. Then the homogeneous mixture obtained was put into an alumina crucible and calcined in a muffle furnace at the temperature of 1200 ℃ for 6 h, and finally the sample was ground thoroughly into powder for measurement after being cooled down to room temperature.

The phase purity of prepared samples were performed on a Rigaku D/MAX-2400 powder X-ray diffractometer (XRD) with Ni-filtered Cu Kα radiation (λ= 1.54178 Å) operated at 40 kV and 60 mA. The 2θ ranges from 10 ~ 80° with the scanning step of 0.02°. The emission and excitation spectra were recorded using an FLS-920T fluorescence spectrophotometer equipped with a 450W Xe light source. The CIE chromaticity coordinates of all samples were calculated by “ZolixColorConvert 1.0” program (Beijing Zolix Instruments Co., Ltd.). All the measurements were performed at room temperature.

Results and Disdussion

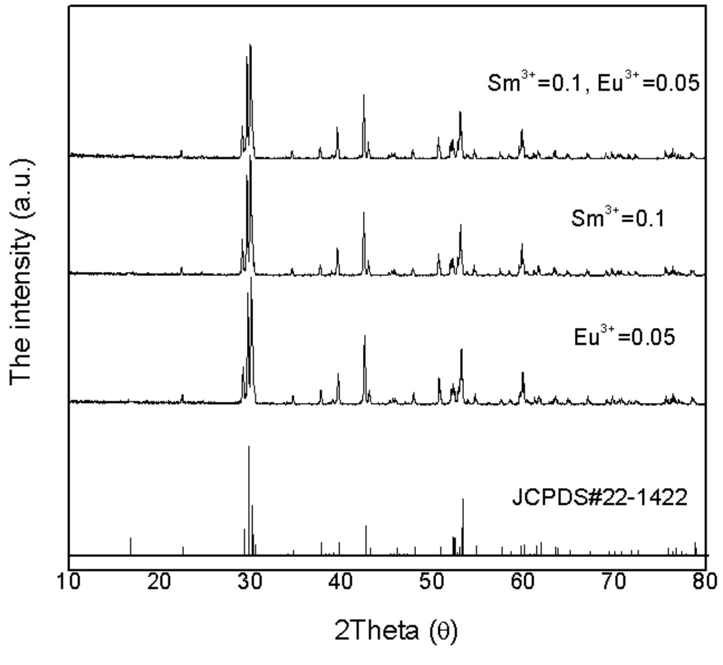

Figure 1. The XRD patterns of $Sr_{1.95}CeO_4$: 0.05Eu^{3+}, $Sr_{1.9}CeO_4$: 0.1Sm^{3+} and $Sr_{1.85}CeO_4$: 0.05Eu^{3+},0.1Sm^{3+} samples. The standard data of Sr_2CeO_4 (JCPDS NO.22-1422).

In order to characterize the phase purity and crystallinity of the as-prepared powder samples, the XRD patterns for all samples were examined. The XRD patterns of $Sr_{1.95}CeO_4$: $0.05Eu^{3+}$, $Sr_{1.9}CeO_4$: $0.1Sm^{3+}$ and $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$, 0.1 Sm^{3+} samples are shown in Fig.1. All of the diffraction peaks were found to be well matched with the JCPDS no. 22-1422, which indicates that no impurity phase is present and the Sr^{2+} can be partly replaced by Eu^{3+} and Sm^{3+} without change of crystal structure. Besides, the XRD patterns for all other samples are the same and no extra diffraction peaks are observed in this paper. Substitution of the Ca^{2+} sites with the trivalent rare-earth ions Eu^{3+} (Sm^{3+}) results in a positive charge $Re^{\bullet}_{Ca}$ in the lattice. In general, according to the Kröger - Vink defect notation [15], the positive charges can be compensated by either cation vacancies V_M'' , or oxygen interstitials $O_i^{\cdot\cdot}$, and the negative charges can be compensated by oxygen vacancies $V_O^{\cdot\cdot}$ in the lattice. In this case, extra positive charge $Eu^{\bullet}_{Ca}$ ($Sm^{\bullet}_{Ca}$), can be compensated by the lattice calcium ion vacancy in Sr_2CeO_4: Eu^{3+}(Sm^{3+}).

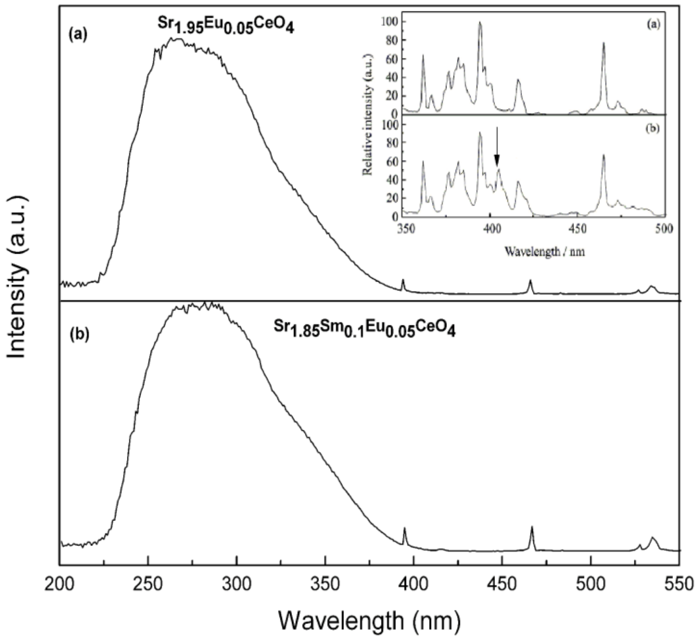

Figure 2. (a) The excitation spectra of $Sr_{1.95}CeO_4$: $0.05Eu^{3+}$ (λ_{em}=614 nm); (b) The excitation spectra of $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$, 0.1 Sm^{3+} (λ_{em}=614 nm). (The inserted figure shows the 350 ~ 500 nm enlarged excitation spectra)

The photoluminescence properties of Sr_2CeO_4: $Eu^{3+}$and Sr_2CeO_4: Eu^{3+}, Sm^{3+} phosphors were measured. Fig. 2 presents that the excitation spectrum of (a) $Sr_{1.95}CeO_4$: $0.05Eu^{3+}$ and (b) $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$,$0.1Sm^{3+}$ phosphors monitored with the 614nm emission consists of a broad band with a maximum at 289 nm and some sharp lines between 350 and 550 nm at room temperature. The broad band centered at 289nm is assigned to the contribution of charge transfer (CT) transition from oxygen to cerium ($O^{2-}\rightarrow Ce^{4+}$), the sharp peaks ranging from 340nm to 450nm corresponding to the f – f transitions of Eu^{3+} and Sm^{3+} ions. Among them, relative to the broadband excitation, the f - f transition absorption peaks are very weak, it's almost impossible to observe. Therefore, the inserted figure shows the 350 ~ 500 nm enlarged excitation spectra of (a) $Sr_{1.95}CeO_4$: $0.05Eu^{3+}$ and (b) $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$, 0.1 Sm^{3+} phosphors. We could see that the most strongest excitation peak at 394 nm ($^7F_0$--$^5L_6$ transition of Eu^{3+}) and the stronger peak at 466 nm ($^7F_0$--$^5D_2$ transition of Eu^{3+}). As shown in the inset of Fig. 2(b), In the case of $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$, 0.1 Sm^{3+}, the excited band about 400 nm was broaden and enhanced because of a extra small sharp excitation peak at 404 nm ($^6H_{5/2}$--$^4F_{7/2}$ transition of Sm^{3+}), these wavelength make the excitation intensity during NUV relatively strong and make the phosphors suitable to be used for NUV excitation. Therefore, Sm^{3+}, Eu^{3+} co-doped Sr_2CeO_4 phosphors is suitable for NUV light wavelength conversion phosphors.

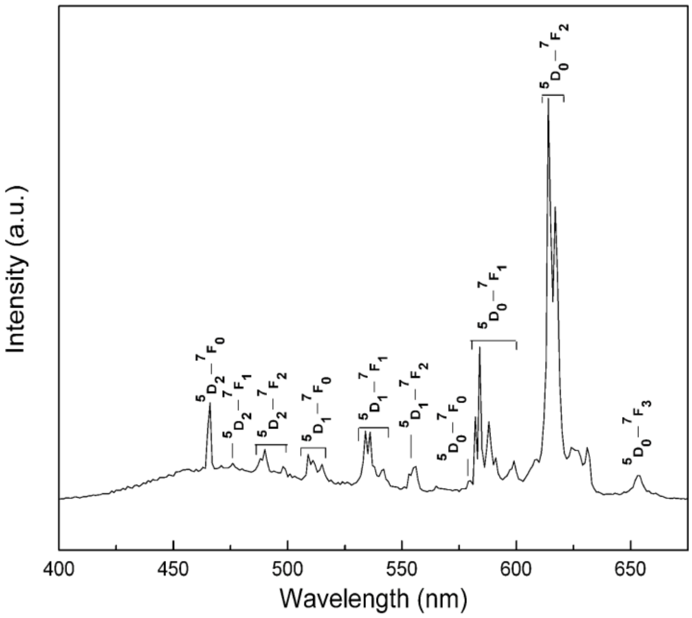

Figure 3. The Emission spectra of $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$, $0.1\ Sm^{3+}$ (λ_{ex}=394 nm)

Fig. 3 shows the emission spectrum of $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$, $0.1\ Sm^{3+}$ phosphor excited at 394nm. From the emission spectra, we could see that there is no emission peak of Sm^{3+} in the emission spectrum, which is mainly the characteristic emission of Eu^{3+}. The emission spectrum of $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$,$0.1Sm^{3+}$ is composed of characteristic emission of Eu^{3+} intra-$4f^6$ sharp lines in the blue, green and red regions, they are assigned to the transitions between the $^5D_0$, $^5D_1$ and $^5D_2$ excited states and $^7F_{0–3}$ ground states. Among all the emission transitions, the hypersensitive electric dipole transition at 614 nm ($^5D_0\rightarrow^7F_2$) was found to be prominent, but other characteristic transitions show the weaker spectral lines. In general, the existence of such a transition from higher levels ($^5D_1$, $^5D_2$)depends on the type of matrix lattice. Usually, it is difficult to observe the transition emission from excited state $^5D_2$, $^5D_1$, this is because among all the excited state of Eu^{3+} ion, the energy gaps between two neighboring $^5D_2$, $^5D_1$, $^5D_0$ excited state levels is relatively small, $\Delta E_1(^5D_2\text{--}^5D_1)\approx 2300cm^{-1}$, $\Delta E_1(^5D_1\text{--}^5D_0)\approx 1733cm^{-1}$[16]. It is easily that efficient electrons relaxation from higher $^5D_2$ and $^5D_1$ excited states levels to the lower $^5D_0$ level and emit characteristic light of $^5D_0$ excited states. It is reported that Sr_2CeO_4 is a special kind of matrix, and its maximum vibration frequency of lattice is lower($<600\ cm^{-1}$) [17,18]. When the Eu^{3+} is doped, the lower lattice vibrational energy is not enough to fully couple the transition from $^5D_1$ to $^5D_0$, so the transition emission of higher $^5D_1$ excited state energy appears. Table1 gives the specific attribution of emission peaks in emission spectra. The dominating emissions peak is around at 614 nm corresponding to the transitions $^5D_0\rightarrow^7F_2$ of Eu^{3+} ion. In addition, From the emission spectra of Eu^{3+} and Sm^{3+} co-doped sample, we could see that there is no emission peak of Sm^{3+} in the emission spectrum, which is mainly the characteristic emission of Eu^{3+}. The preliminary analysis is that there is a certain energy transfer between Sm^{3+} and Eu^{3+}.

In order to further show that there is a energy transfer in Eu^{3+} and Sm^{3+} co-doped sample, we analyzed the emission spectrum under 404 nm excitation. From the excitation spectrum of $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$,0. $1Sm^{3+}$(in the inserted Fig. 2(b)) , it is found that a extra small sharp excitation peak at 404 nm ($^6H_{5/2}\text{--}^4F_{7/2}$ transition of Sm^{3+}).Therefore, we measured the emission spectra of $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$,$0.1Sm^{3+}$ and $Sr_{1.95}CeO_4$: $0.05Eu^{3+}$ under 404 nm excitation, which the emission spectrum are similar to that of the emission spectrum under the excitation of 394 nm(in Fig. 3). In $Eu^{3+}$and Sm^{3+} co-doped sample, the emission spectra under 404 nm excitation is the same as that of the Eu^{3+} single doped sample, indicating that the co-doped sample can be excited efficiently by 404 nm corresponding to the $^6H_{5/2}$--$^4F_{7/2}$ transition of Sm^{3+} ion, the emission from Characteristic transitions of Eu^{3+} is also observed . This can be considered as a clear evidence of energy transfer from Sm^{3+} to Eu^{3+} ion. The relative emission intensity of the Eu^{3+}/Sm^{3+} co-doped systems at 614 nm is about 3 times that of the Eu^{3+} single-doped systems. It states that the Sm^{3+} ions can absorb and transfer energy to Eu^{3+} ions efficiently.

Table1 Attribution of Eu^{3+} emission peaks in phosphor of $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$, $0.1Sm^{3+}$

Emission peak/ nm	Attribution	Emission peak/ nm	Attribution
466	$^5D_2$-$^7F_0$	556	$^5D_1$-$^7F_2$
490	$^5D_2$-$^7F_2$	584	$^5D_0$-$^7F_1$
509	$^5D_1$-$^7F_0$	614	$^5D_0$-$^7F_2$
534	$^5D_1$-$^7F_1$	653	$^5D_0$-$^7F_3$

A simple model of the process of the energy transfer from Sm^{3+} to Eu^{3+} is illustrated in Fig. 4. Under the excitation of 404 nm, Sm^{3+} in the ground state ($^6H_{5/2}$) are excited to the excitd state($^4F_{7/2}$), and then the non-radiatively relaxation of the $^4G_{5/2}$ level is populated. Some of the excited Sm^{3+} ions act as sensitizers to transfer their energy to Eu^{3+} ions. As a result, the Eu^{3+} ions are sensitized to show the characteristic emissions of $^5D_0 \rightarrow {}^7F_2$ transition, which gives rise to red visible light. The reason why $Sm^{3+} \rightarrow Eu^{3+}$ energy transfer occurs is that the $^4G_{5/2}$ level of the lowest excited state energy level of Sm^{3+} is 600 cm^{-1} higher than that of Eu^{3+} ($^5D_0$). Therefore, through the energy transfer of $Sm^{3+} \rightarrow Eu^{3+}$, the $^5D_0$-$^7F_2$ emission of Eu^{3+} is obviously enhanced.

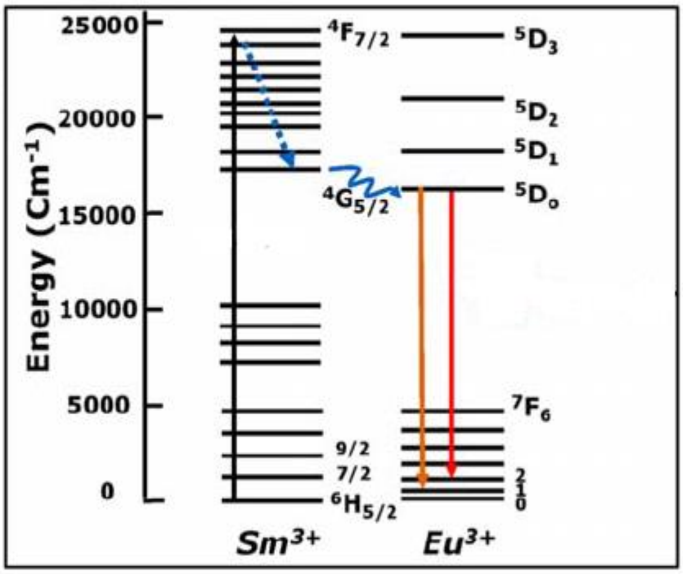

Figure 4. Energy level diagram of Eu^{3+}/Sm^{3+} single and schematic diagram of Sm^{3+} - Eu^{3+} energy transfer process in Sr_2CeO_4 phosphors.

On the whole, the luminous efficiency of $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$,$0.1Sm^{3+}$ phosphor under the excitation of 404 nm was obviously improved, which is about 3 times of that of the single doped $Sr_{1.95}CeO_4$: $0.05Eu^{3+}$. The CIE chromaticity coordinates of $Sr_{1.85}CeO_4$: $0.05Eu^{3+}$,$0.1Sm^{3+}$ phosphor is calculated as (0.65, 0.32) by “Zolix Color Convert” program, which is closer to the NTSC standard red light values of (0.67, 0.33). These results showed that the Sr_2CeO_4: Eu^{3+},Sm^{3+} phosphor could be used as a candidate material for NUV-LED with red phosphors.

Conclusions

In summary, a novel red-emitting phosphor Sr_2CeO_4: Eu^{3+}, Sm^{3+} has been prepared by conventional high-temperature solid-state method. The X-ray diffraction, photoluminescence properties were investigated in detail. For the Eu^{3+}/Sm^{3+} exhibits strong absorption at 395 nm/405 nm in many matrices, double doped phosphors Sr_2CeO_4: Eu^{3+}, Sm^{3+} not only broaden and enhance the absorption band at ~ 400 nm, but also because of the energy transfer from Sm^{3+} to Eu^{3+}, the luminous efficiency of phosphor is greatly improved. Under the excitation of NUV, the luminescence intensity of the phosphor $Sr_{1.85}CeO_4$: 0.05Eu^{3+}, 0.1Sm^{3+} was 3 times higher than that of the single doped phosphor $Sr_{1.95}CeO_4$: 0.05Eu^{3+}. All the results implying that the phosphors Sr_2CeO_4: Eu^{3+}, Sm^{3+} has potential research value on white-LEDs.

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