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A NEW SINGLE-COMPONENT $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}:\text{Dy}^{3+}$, Eu^{3+} POTENTIAL PHOSPHOR FOR WHITE-LIGHT EMITTING DIODES: LUMINESCENCE PROPERTIES, ENERGY TRANSFER AND MULTICOLOR LUMINESCENCE

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ABSTRACT

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In this study, novel single-component $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}:\text{Dy}^{3+}$, Eu^{3+} phosphor has been successfully prepared by high temperature solid state reaction. The crystal structure, luminescent property, energy transfer and multicolor emission behavior were investigated in detail. The structure was characterized by X-ray diffraction (XRD) and the results indicate that the as-prepared samples are of pure orthorhombic phase of $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$ and Dy^{3+} and Eu^{3+} are totally incorporated into the host lattice of $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$. The Dy^{3+} or Eu^{3+} single doped samples exhibit strong yellow and red emissions, originating from the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ transition of Dy^{3+} and the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_j$ ($j=0, 1, 2, 3$) transitions of Eu^{3+} and the optimal concentration of Dy^{3+} and Eu^{3+} ions in $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$ were determined to be 5 mol% and 11 mol%, respectively. Meanwhile, the energy migration from Dy^{3+} to Eu^{3+} in co-doping samples has been confirmed by the excitation and emission spectra and the process was reported in detail. Based on the energy transfer, under the excitation of 344 nm, the emitting color can change from yellow to orange red by adjusting the relative doping concentration of Dy^{3+} and Eu^{3+} ions, indicating that the phosphors $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}:\text{Dy}^{3+}$, Eu^{3+} with tunable multicolor emissions may have potential application in pc-white LEDs.

KEYWORDS

 $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}:\text{Dy}^{3+}$, Eu^{3+} , Energy transfer, Multi-color emission, WLED

1. INTRODUCTION

In recent years, with the issues of the energy and environmental becoming increasingly prominent, white-light-emitting diodes (WLEDs) have been widely studied and used in the lighting and display fields due to their special superiorities of saving energy, long lifetime, reliability, environmental friendly and so on [1-3]. Nowadays, in several ways to assemble WLEDs, the most prevalent strategy is based on YAG: Ce^{3+} as a kind of broadband yellow phosphor coated on a blue InGaN chip, however, because of the innate lack of red-emission, this combination usually has the problems of low color rendering index (CRI) and high correlated color temperature (CCT) [4,5]. Another method is to combine n-UV LED with blue, green and red phosphors which is considered to be more stable and flexible. But the shortcomings of the reabsorption of blue light by red and green phosphors appear, resulting in lower external quantum luminous efficiency of the resulting w-LEDs. Based on this situation, the single-phase phosphor-converted UV WLEDs can overcome these drawbacks because it possesses some surprisingly favorable properties, such as tunable CIE chromaticity coordinates, excellent R_a values and color stability, etc. Therefore, an increasing number of researchers have paid attention to studying and developing full-color emitting single-phase phosphors [6-10].

Co-doping sensitizer and activator into the same host based on the energy transfer is one of the approaches to produce white light or color-tunable emissions from single phase phosphors. Many materials can be the matrix, such as phosphates, lanthanide-doped oxides and fluorides, among these materials, the aluminosilicate (such as $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$) is regarded as an interesting and highly-focused host luminescent material for rare earth ions emission due to its excellent chemical and thermal stability and proper crystal field to promote luminescence [11-13]. Among various RE

trivalent ions, dysprosium (Dy^{3+}) is well known for its emission in the yellow and blue regions corresponding to the ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{13/2}$ and ${}^4\text{F}_{9/2} \rightarrow {}^6\text{H}_{15/2}$ transitions, respectively. If the ratio of blue to yellow emission is appropriate, white emission can be attained by using Dy^{3+} ions alone [14,15]. But the combination of blue and yellow emissions lacks the red part, the Eu^{3+} that emits red light corresponding to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ transition can be introduced [16]. Thereby, it is feasible to produce Dy^{3+} and Eu^{3+} co-activated white light or tunable color phosphors. At present, Dy^{3+} and Eu^{3+} co-doped single-phase phosphors have been vigorously studied and reported, such as $\text{Na}_3\text{Gd}(\text{PO}_4)_2$, BaLa_2WO_7 , $\text{BaCa}_2\text{Y}_6\text{O}_{12}$ and $\text{Ca}_2\text{La}_8(\text{GeO}_4)_6\text{O}_2$ [1,8,17,18]. However, their work have solely focused on the multicolor emissions based on the energy transfer [19,20]. Hence, different with previous studies, by taking into consideration the characteristic emissions of dysprosium and europium ions, it is expected that multicolor emissions could be achieved in $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$ system by adjusting different excitation wavelengths and properly designed activator contents. Dy^{3+} - Eu^{3+} co-doping aluminosilicate $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$ single-phase phosphor is novel and its synthetic process is simple and convenience. Meanwhile, the luminosity is ideal and energy transfer in $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}:\text{Dy}^{3+}$, Eu^{3+} have not been yet investigated up to now.

In this work, we first reported a novel single phase $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}:\text{Dy}^{3+}$, Eu^{3+} phosphor prepared through a simple high temperature solid state method. The crystal structure, luminescence properties, energy transfer and color tunable luminescence of the phosphors were studied. The energy transfer from Dy^{3+} to Eu^{3+} in $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$ (following for short as CAMSO) system were investigated in detail and the mechanisms are also discussed for the energy transfer behavior. Finally, the results indicate that this phosphor can be effectively excited by UV (about 344nm)

light and emit visible light from yellow to orange red by altering the concentration ratio of Dy^{3+} and Eu^{3+} , and it may have potential applications in white LEDs as a promising single-phase color-tunable phosphor.

2. EXPERIMENTAL

A series of single-phased CAMSO: Dy^{3+} , Eu^{3+} phosphors were synthesized by high temperature solid-state reaction. The raw materials CaCO_3 (A.R.), Al_2O_3 (A.R.), MgO (A.R.), SiO_2 (A.R.) were obtained from the Beijing Chemical Reagent Research Institute of China and spectrographically pure Dy_2O_3 (99.95%), Eu_2O_3 (99.99%) were supplied by Shanghai Yuelong Non-Ferrous Metals Limited of China. These raw reactants were quantified based on the stoichiometric molar ratio and then mixed in an agate mortar by grinding. The powder after mixing was placed in a small corundum crucible and sintered in a tubular furnace at 1380 °C for 2 h in air atmosphere, and slowly cooled down to room temperature.

The powder X-ray diffraction patterns (XRD) were recorded by powder X-ray diffractometer (RigakuD/Max-BII), using $\text{Cu K}\alpha$ radiation. The excitation and emission spectra were recorded by a Jobin Yvon FluoroMax-4 equipped with a 150W xenon lamp as the excitation source. All the experiments were performed at room temperature.

3. RESULTS AND DISCUSSION

The crystal structure of CAMSO belongs to a orthorhombic space group with a relatively large unit cell, and the lattice parameters are $a=27.64 \text{ \AA}$, $b=10.802 \text{ \AA}$, $c=5.124 \text{ \AA}$ and $V=1529.9 \text{ \AA}^3$, respectively. Figure 1 represents the crystal structure and cation polyhedral arrangements of CAMSO. The structure contains twelve AlO_4 , twelve $(\text{Mg,Al})\text{O}_4$ and eight $(\text{Al,Si})\text{O}_4$ tetrahedra with mean M-O (M=Mg/Al, Si/Al, or Al) distances of 1.76, 1.79 and 1.71 \AA , respectively. AlO_4 and $(\text{Al,Si})\text{O}_4$ tetrahedra are linked through corners to form a network of five-membered rings, similar to those found in gehlenite and $5\text{Ca}_0.3\text{Al}_2\text{O}_3$. These differ in the propagation of the five-membered rings of MO_4 tetrahedra. While in $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$, MO_4 tetrahedra are connected into infinite strips of five-membered rings in the b direction separated by chains of $(\text{Mg,Al})\text{O}_4$ tetrahedra, the five-membered rings in the last two compounds extend into infinite networks. Twelve Ca^{2+} ions in $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$ are coordinated by eight O^{2-} , and eight Ca^{2+} by six O^{2-} anions [21].

In order to identify the composition and phase purity of as-prepared products, XRD measurements were carried out. Figure 2 shows the XRD patterns of CAMSO: Dy^{3+} , Eu^{3+} phosphors with different Dy^{3+} and Eu^{3+} concentrations as well as the standard diffraction lines of $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$ (JCPDS no.350133). It can be seen that all the diffraction peaks of these samples correspond to the JCPDS standard pattern (JCPDS no.350133) and no other phases or impurities appear. This implies that the pure phase powder was obtained and the Dy^{3+} and Eu^{3+} ions can be dissolved into this host without producing any other phase. The approximate ionic radii of Dy^{3+} (0.0908 nm) and Eu^{3+} (0.0950 nm) are all similar to that of Ca^{2+} (0.100 nm) so the Dy^{3+} and Eu^{3+} ions preferably occupies the Ca^{2+} ions rather than Mg^{2+} (0.072 nm) [22]. Some small shifts in the diffraction patterns relative to the standard diffraction pattern of JCPDS no. 35-0133 can be ascribed to the differences of ionic radius between Ca^{2+} and Dy^{3+} as well as Eu^{3+} . When the larger Ca^{2+} (0.100 nm) ions were substituted by the smaller Dy^{3+} (0.0908 nm) ions in the phosphor, the diffraction peaks are slightly shifted to a higher degree, in accordance to the Bragg equation: $\lambda=2d\sin\theta$ [23].

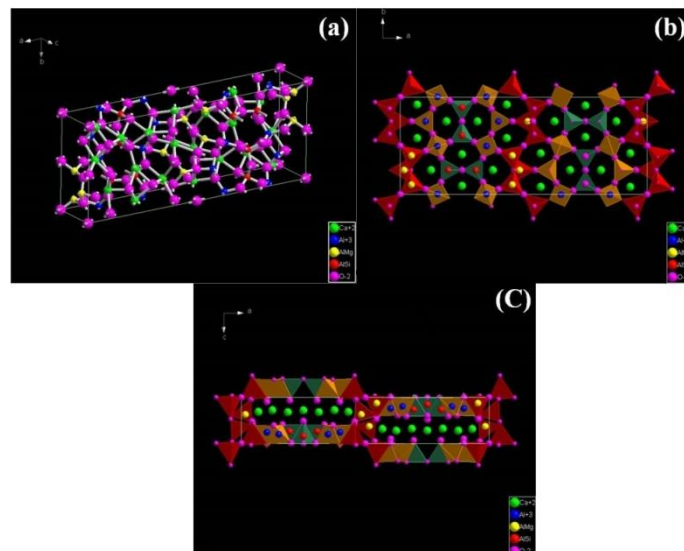


Figure 1: Crystal structure and cation polyhedral arrangements of CAMSO host

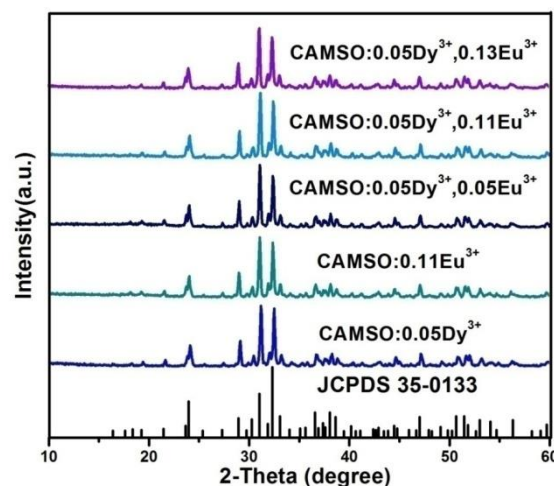


Figure 2: The XRD patterns of $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}:\text{Dy}^{3+}$, $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}:\text{Eu}^{3+}$ and $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}:\text{Dy}^{3+}$, Eu^{3+} samples. The standard data of $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$ (JCPDS no. 350133) is given as reference

The photoluminescence excitation and emission spectra of CAMSO:5% Dy^{3+} sample are displayed in Figure 3a. The excitation spectrum monitored with 475 nm emission (${}^4\text{M}_{21/2}\rightarrow{}^6\text{H}_{11/2}$) is made up of a sharp excitation band at 344 nm (the strongest peak) and several other bands centered at 294, 320, 364 and 384 nm, which are corresponding to the transitions of Dy^{3+} from the ground state ${}^6\text{H}_{15/2}$ to the excited state ${}^4\text{M}_{15/2}$, ${}^4\text{D}_{7/2}$, ${}^4\text{M}_{17/2}$, ${}^4\text{I}_{11/2}$, ${}^4\text{I}_{13/2}$, respectively. These excitation peaks indicate that the phosphor can forcefully absorb ultraviolet and blue light to obtain Dy^{3+} emission. Under the excitation of 344 nm, the emission spectrum of CAMSO:5% Dy^{3+} covering the region from 450 nm to 700 nm contains two dominating emission bands, whose peaks are at 475 nm (blue) and 577 nm (yellow), attributing to the Dy^{3+} transitions of the magnetic dipole (${}^4\text{F}_{9/2}\rightarrow{}^6\text{H}_{15/2}$) and electric dipole transitions (${}^4\text{F}_{9/2}\rightarrow{}^6\text{H}_{13/2}$), respectively [24].

It can be seen that the emission at 475 nm lines is more intense than that at 577 nm lines, namely, the intensity of blue emission is greater than that of yellow emission. It is well known that the hypersensitive transition is strongly influenced by the outside environment surrounding Dy^{3+} , and the magnetic dipole transition is insensitive to the crystal field around the Dy^{3+} ions. When Dy^{3+} is located at a low symmetry site (without inversion symmetry), the yellow emission is dominant in the emission spectrum; when Dy^{3+} is at a high symmetry site (with inversion symmetry), the blue emission is stronger than the yellow emission [25]. The stronger blue emission suggests that the site of Dy^{3+} ions has low symmetry, and this also can be confirmed by the crystal structure of $\text{Ca}_{20}\text{Al}_{26}\text{Mg}_3\text{Si}_3\text{O}_{68}$ in Figure 1.

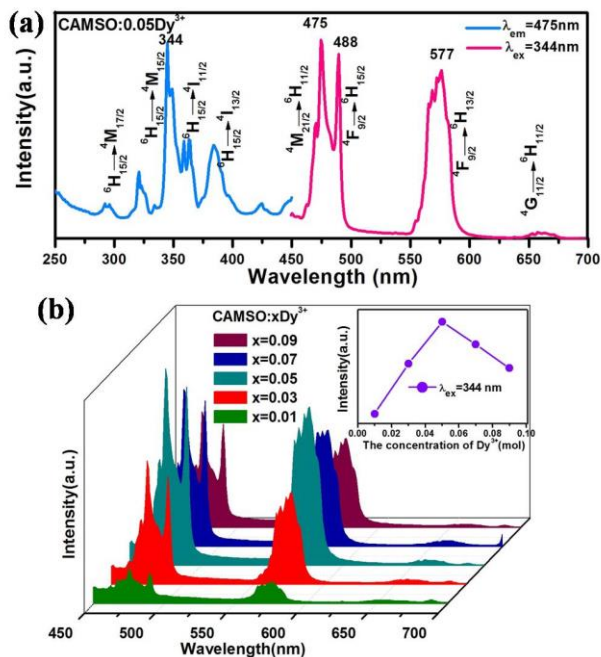


Figure 3: (a) The excitation and emission spectra of CAMSO:0.05Dy³⁺ sample (b) the emission spectra of CAMSO: xDy³⁺ (x=0.01-0.09) samples, the inset exhibits the intensity of Dy³⁺ ion with different Dy³⁺ concentrations

Figure 3b illustrates the PL spectra of a series of CAMSO:xDy³⁺ with different Dy³⁺ concentrations under 344 nm excitation. It can be obviously observed that all emission bands show similar profiles with different relative intensities. Firstly, with the increasing of Dy³⁺ doping content, the emission intensity of the samples increases continuously, the best luminous concentration was at x=5%, then decreases further when the doping content of Dy³⁺ ions exceeds 5 mol% due to the concentration quenching effect. Therefore, the optimum concentration of Dy³⁺ was determined to be 5 mol%. The energy migration among the activator ions at high concentration triggers the concentration quenching. In this process, the loss of energy increases at a killer or quenching site, so the emission intensity decreases [26].

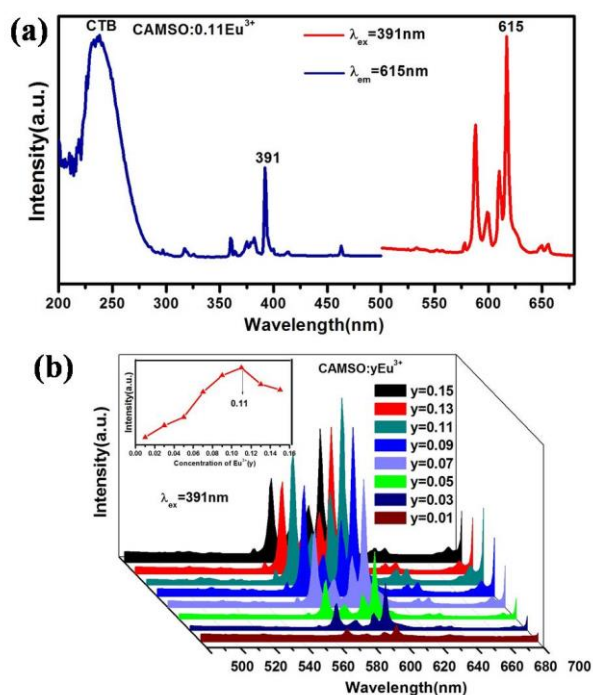


Figure 4: (a) The excitation and emission spectra of CAMSO:0.11Eu³⁺ sample (b) the emission spectra of CAMSO: yEu³⁺ (y=0.01-0.15) samples, the inset exhibits the intensity of Eu³⁺ ion with different Eu³⁺ concentrations

Figure 4a gives the excitation and emission spectra of CAMSO:11%Eu³⁺ samples. From the figure, it can be found that the excitation spectrum monitored at 615 nm consists of a broad band from 200 to 300 nm and a sharp line with a maximum at 391 nm. The broad band is attributed to the charge transfer (CT) band of Eu³⁺-O²⁻ and host and it may include the CT excitation of Eu³⁺ ions and the energy transfer transition from matrix to Eu³⁺ ions. More in-depth, the CT band is due to the transition of electron from the filled 2p levels of oxygen to the 4f orbital of Eu³⁺. The narrow excitation peak at 391 nm is corresponding to the ⁷F₀→⁵L₆ transition of Eu³⁺. When excited at 391 nm, the emission spectrum covering the region from 500 to 700 nm is obtained. In the spectrum, there are several emission bands at 576, 587, 615 and 653 nm which correspond to the characteristic f-f transitions of Eu³⁺, in detail, ⁵D₀→⁷F₀, ⁵D₀→⁷F₁, ⁵D₀→⁷F₂ and ⁵D₀→⁷F₃ respectively [27]. It is clearly observed that the strong emission ascribed to the ⁵D₀→⁷F₂ electric dipole transition (615 nm) becomes strongest among all these peaks, indicating that the sites of Eu³⁺ ions is lack of inversion symmetry. Thereby, the red emission is often dominant in the emission spectrum and the phosphor CAMSO:11%Eu³⁺ shows a bright red light under UV irradiation. The emission spectra of CAMSO: y%Eu³⁺ with different concentrations of Eu³⁺ are shown in Figure 4b. The explanation of the concentration quenching of Eu³⁺ ions is similar to Dy³⁺, please refer to Fig. 4b. The optimal doping contents of Eu³⁺ is determined to be 11%.

In order to further study the tunable color luminescence and energy transfer in Dy³⁺, Eu³⁺ co-doped CAMSO host, the concentration of Dy³⁺ ions is fixed for 5 mol%, a optimized concentration which is chosen based on the results of the PL intensity of Dy³⁺-doped phosphors, a series of CAMSO:5%Dy³⁺, y%Eu³⁺ (y=0, 0.01-0.15) samples have been prepared and their PL spectra are compared in Figure 5a. It can be seen that the emission spectra under the excitation of 344 nm contain the characteristic emissions for both Dy³⁺ and Eu³⁺ ions. As shown in Figure 5a and b, with the increasing of Eu³⁺ contents, the emission intensity of Dy³⁺ ions decrease while the emission intensity of Eu³⁺ ions increase, which implies that the Eu³⁺ ions emission is sensitized by Dy³⁺ ions through the energy transfer. When the Eu³⁺ concentration is beyond 11 mol%, the intensity of the Eu³⁺ emission begins to decrease due to the self-quenching effect which are the interactions between Eu³⁺ ions. The above results demonstrate that tunable color can be realized by adjusting the concentration of Eu³⁺ and the energy transfer from Dy³⁺ to Eu³⁺ exists in the CAMSO host.

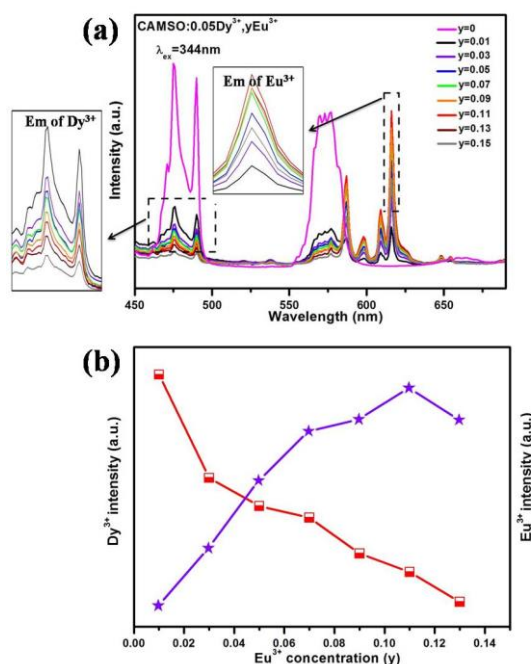


Figure 5: (a) Photoluminescence emission spectra of the CAMSO:0.05Dy³⁺, yEu³⁺ (y=0.01-0.13) samples with different Eu³⁺ doped concentrations (b) dependence of emission intensity on the Eu³⁺ concentration

The CIE 1931 chromaticity coordinates diagram for CAMSO:5%Dy³⁺, y%Eu³⁺ phosphors measured at 344 nm is depicted in Figure 6. It can be seen that with the increasing Eu³⁺ concentration, the chromaticity coordinates value (x, y) vary systematically from (0.388, 0.422) to (0.511, 0.267) because of the different emission components of the Dy³⁺ and Eu³⁺ ascribed to the energy transfer from Dy³⁺ to Eu³⁺. In addition, the corresponding color tone of the samples can change from yellow to orange red light by appropriately adjusting the relative content proportion of Dy³⁺ and Eu³⁺. The phosphors can realize multicolor emission from yellow to orange red light under the excitation with an UV wavelength of 344 nm, which is accessible to UV LEDs. The above results indicate that the CAMSO: Dy³⁺, Eu³⁺ phosphor has potential application value in pc-white LEDs.

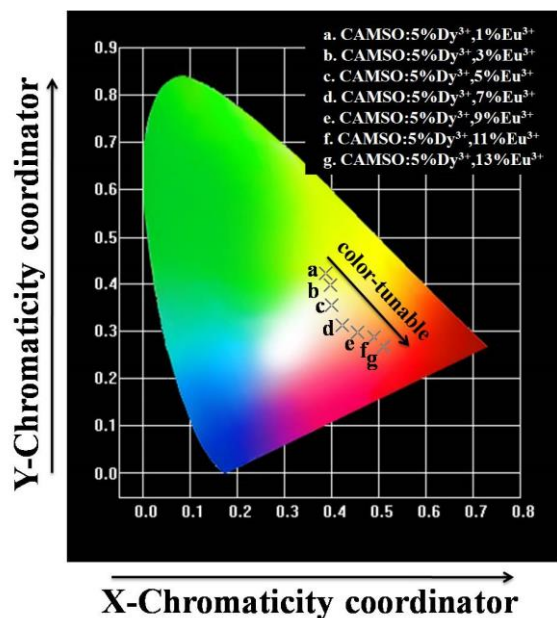


Figure 6: CIE chromaticity diagram of the selected CAMSO:0.05Dy³⁺,yEu³⁺ phosphors under the UV excitation

4. CONCLUSIONS

In general, a series of Dy³⁺ and Eu³⁺ co-doped CAMSO phosphors have been synthesized by solid state reaction and the crystal structure, luminescent property, energy transfer and multicolor emission behavior were investigated in detail. The XRD analyses indicate that Dy³⁺ and Eu³⁺ are totally incorporated into the CAMSO host lattice. The energy transfer process of Dy³⁺→Eu³⁺ has been confirmed in the CAMSO host by the excitation and emission spectra. In addition, the emission color can be tuned from yellow to orange red by adjusting appropriate concentration of Dy³⁺ and Eu³⁺ ions the above results indicate that the single-component phosphors exhibiting color-tunable emissions may have potential application value in pc-white LEDs.

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