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Warm white light emission of apatite-type compound $Ca_4Y_6O(SiO_4)_6$ doped with Dy^{3+}

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ABSTRACT

A series of $Ca_4Y_6O(SiO_4)_6$: $x\%Dy^{3+}$ (x = 1, 3, 5, 7, 9) phosphors were synthesized successfully via a conventional solid-state method at high temperature. The X-ray diffraction results show that all obtained samples are the pure hexagonal crystal structure of the space group $P6_3/m$ (No.176). The blue ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and yellow ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) emissions of $Ca_4Y_6O(SiO_4)_6$:7% Dy^{3+} phosphors are of such a ratio to produce almost perfect white light with CIE coordinates of (0.330, 0.339). The correlated color temperature is about 5600 K, close to that of the midday sunlight (5500 K). In addition, both the emission intensity and the CIE coordinates exhibit an excellent thermal stability in the temperature range of RT ~ 300 °C. Our study illustrates that $Ca_4Y_6O(SiO_4)_6$:7% Dy^{3+} may serve as potential warm white lighting phosphors in NUV-based solid state lighting and optical display applications.

1. Introduction

The problems of energy crisis, greenhouse effect, PM2.5 and ecological environment are getting more serious day after day, which have become hard nuts to crack for today's international community [1–4]. Meanwhile, changing the way of energy acquisition and improving the energy utilization rate are the keys to solve those problems [1,4–9]. Up to Now, lighting and displays have accounted for a growing share of the total energy consumption [7,8]. Owing to merits of energy savings, free of mercury pollution, long lifetimes, short response time, and high energy efficiency, etc. [8–16], the promising phosphor-converted white light-emitting diodes (WLEDs) have been considered to be important light sources. To obtain high-performance WLED lighting, the development of highly efficient fluorescent materials is one of the core issues.

In general, white light generation can be realized by three main ways [14–20]: (1) the combination of red-green-blue (RGB) tricolor LEDs, however, fabrication is rather complicated; (2) utilizing a GaN-based blue chip with $Y_3Al_5O_{12}$:Ce^{3+} yellow phosphor, but suffering from a poor color rendering index due to lack of red–light component; (3) utilizing a ultraviolet-LED chip coated with three phosphors which emitting red, green, and blue light, respectively, where excellent color rendering indexes can be achieved. Nevertheless, these multi-phase phosphors with different decay time and reabsorption of emission colors may lead to a decrease in luminous efficiency for practical application. Therefore, design of single-composition white-emitting phosphors, with excellent color rendering indexes and simple design and control, pumped by near-ultraviolet (NUV) or blue chips is of significance for WLEDs.

Among rare earth ions, Dy^{3+} has been extensively studied to generate white light in various hosts [20–24] owing to its two main emission parts: the blue band (460–500 nm) corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and the yellow band (550–600 nm) due to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. Furthermore, the hypersensitive $^4F_{9/2} \rightarrow {}^6H_{13/2}$ electric dipole transition is sensitive to the chemical environment surrounding of Dy^{3+} ion, so the yellow to blue (Y/B) emission intensity ratio ($^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition) / ($^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition) also reveals the coordination surroundings of the Dy^{3+} ion to some extent, and it is possible to obtain near white light emission by controlling the Y/B intensity ratio through adjusting the lattice structure of the luminescent materials.

As a type of silicates, $Ca_4Y_6O(SiO_4)_6$ shows excellent thermal and chemical stability as well as very low harm to the environment and human health. And this host lattice consists of two cationic sites, that is, 4*f* site with C_3 point symmetry occupied by a 9-fold coordinated Ca^{2+} and 6*h* site with C_s point symmetry occupied by 7-fold coordinated Y^{3+}. Both sites are suitable and easily accommodate a great variety of rare earth and transitional-metal ions. Up to now, $Ca_4Y_6O(SiO_4)_6$: Re (Re = Eu^{3+}, Ce^{3+}, Eu^{2+}, Mn^{2+}, Pb^{2+}, Tb^{3+}, Dy^{3+}) [25–28] have been reported, and the excellent performance for the various rare earth ions are all unfolded in this matrix. For example, in 2014, Wang et al. [25]

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found that the emission intensity of $Ca_4Y_6O(SiO_4)_6$: Eu^{3+} (the CIE coordinates locate about (0.636,0.338)) is stronger than that of the commercial Y_2O_2S: Eu^{3+} phosphors. And in 2015, Li et al. [26] demonstrated that $Ca_4Y_6O(SiO_4)_6$: Eu^{2+}, Mn^{2+} can be effectively excited by 432 nm blue LED, and produce warm white emission (CIE coordinates (0.336, 0.319), correlated color temperature (CCT) 4326 K and color rendering index (R_a) 86) by energy transfer from Eu^{2+} to Mn^{2+}, with QE about 39.6%. In 1995 and 2011, Lin et al. [27] and Yang et al. [28] investigated the luminescent characteristics (including excitation and emission spectra, the ratio of the blue ($^4F_{9/2} \rightarrow {}^6H_{15/2}$) and yellow ($^4F_{9/2} \rightarrow {}^6H_{13/2}$) emissions varied with increasing Dy^{3+} concentration, and the emission chromaticity) of $Ca_4Y_6O(SiO_4)_6$:Dy^{3+} phosphors.

Based on the work mentioned above, to get closer to the application, in our work, a series of $Ca_4Y_6O(SiO_4)_6$: x%Dy^{3+} phosphors were synthesized, and the crystal structures, the excitation and emission intensities, concentration quenching, CIE chromaticity coordinates varied with the concentration, quantum yield, thermal stability, the activation energy for thermal quenching, even the CIE chromaticity coordinates varied with the temperature of $Ca_4Y_6O(SiO_4)_6$: Dy^{3+} phosphors were all studied in detail. These results demonstrate that $Ca_4Y_6O(SiO_4)_6$: 7% Dy^{3+} may serve as potential white emitting phosphors to get the warm white light in NUV-based solid state lighting and optical display applications.

2. Experimental

A series of $Ca_4Y_6O(SiO_4)_6$: x mol%Dy^{3+} (x = 0, 1, 3, 5, 7, 9) phosphors were synthesized via a high-temperature solid-state method. The raw materials $CaCO_3$ (A. R. grade), SiO_2 (A. R. grade), Y_2O_3 (99.9%) and Dy_2O_3 (99.99%) are weighted accurately in stoichiometric proportion, and then transferred to an agate mortar following by careful grinding for half an hour. The mixture of fine powders was calcined in the Muffle furnace at 1000 °C for 4 h in an atmosphere. After the samples were cooled down to room temperature (RT), they were ground again and sintered at 1450 °C for 8 h. Finally, the powder samples were reground and collected for characterization.

The phase formation was determined by X-ray diffraction (XRD) in an X-Ray Diffractometer (Persee, XD-2) with Cu-Kα (λ = 1.5406 Å) at 36 KV and 20 mA, and a scan rate of 2 °/min was applied to record the patterns in the 2θ range from 25° to 55°. The photoluminescence excitation (PLE), photoluminescence (PL) spectra and the fluorescence decay were recorded by a FLS920 fluorescence spectrophotometer (Edinburgh Instrument Ltd., Livingston, UK) equipped with a 450 W xenon lamp or a pulsed xenon lamp as the light source, and a Shimidazu R9287 photomultiplier as the detector. Quantum yields (QY) of the samples were measured at RT with the aid of the integrating sphere and the FLS920 fluorescence spectrophotometer. The powder samples were placed into the integrating sphere and excited by the 450 W xenon lamp. To identify the thermal stability of the samples for the application in WLED, the temperature-dependent PLE and PL were collected by the FLS920 fluorescence spectrophotometer equipped an external home-made temperature controller.

3. Results and discussion

The XRD patterns for all as-prepared $Ca_4Y_6O(SiO_4)_6$: x%Dy^{3+} (x = 0, 1, 3, 5, 7, 9) phosphors are characterized at RT in Fig. 1(a). The diffraction peaks for all the samples are similar to each other and agree well with the Joint Committee on Powder Diffraction Standards (JCPDS) file 27-0093 ($Ca_4Y_6O(SiO_4)_6$), which indicates that all the samples are of single pure phase. What is more, in view of the similar ion radius and valence, Dy^{3+} ions (ion radius: 90.8 pm) are expected to substitute Y^{3+} (ion radius: 90 pm) sites. Therefore, as showed in Fig. 1(a), it is noted that the diffraction peaks (2θ) hardly present any shift comparing with those of the standard PDF card. $Ca_4Y_6O(SiO_4)_6$ has a hexagonal crystal structure, with a space group $P6_3/m$ (No.176), and cell parameters a = b = 0.9356 nm, c = 0.6793 nm, α = β = 90°, and γ = 120°. As one kind of silicates with oxy-apatite structure, $Ca_4Y_6O(SiO_4)_6$ presents an excellent thermal and chemical stability as well as the stabilization of ionic charge, which have ensured their efficiency as luminescent host. The structural schematic representation of $Ca_4Y_6O(SiO_4)_6$ host is illustrated in Fig. 1(b). It is seen that the host lattice consists of two cationic sites: (1) Ca^{2+}: the 9-fold coordinated $4f$ site with C_3 point symmetry; (2) Y^{3+}: the 7-fold coordinated $6h$ site with C_s point symmetry. Both sites are suitable and easily accommodate a great variety of rare earth. While Dy^{3+} ions (90.8 pm) are more likely to occupy $6h$ site with C_s point symmetry of Y^{3+} (90 pm) rather than $4f$ site of Ca^{2+} (99 nm) because of both ion radius and charge mismatch. Furthermore, lack of space inversion symmetry in $6h$ site with C_s point symmetry leads to mixing in the $(4f)^N$ Stark energy levels of compositions with opposite symmetry due to odd-parity crystal-field interactions, which will benefit $4f^N$-$4f^N$ radiative transitions.

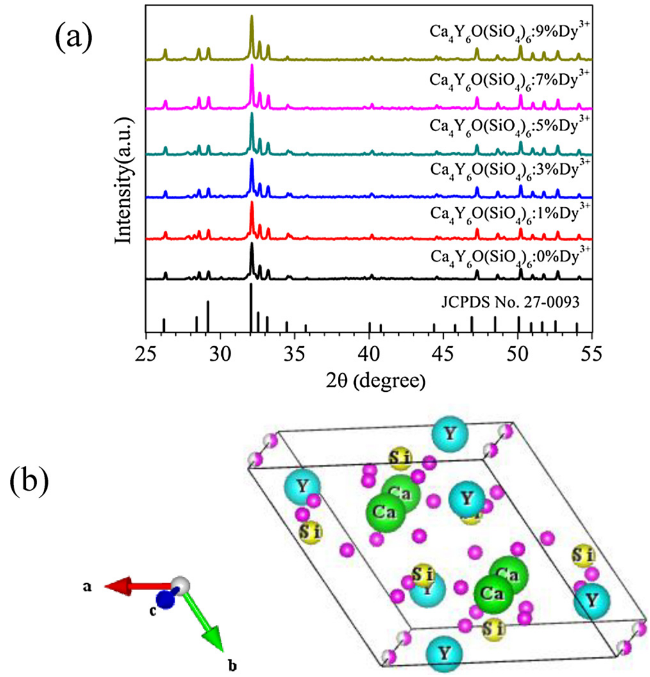

Fig. 1. (a) The XRD patterns of $Ca_4Y_6O(SiO_4)_6$: x%Dy^{3+} (x = 0, 1, 3, 5, 7, 9) phosphors, and (b) its schematic view of the structure and coordination environments.

The inset in Fig. 2 shows PLE (240 nm – 440 nm) and PL (450 nm – 600 nm) spectra of $Ca_4Y_6O(SiO_4)_6$ matrix. The two bands (a: peaked at 294 nm, ranging from 240 nm to 350 nm; b: peaked at 366 nm, ranging from 300 nm to 440 nm) of PLE spectra can be obtained by the Gaussian Fitting. The shapes of emission spectra of $Ca_4Y_6O(SiO_4)_6$ matrix are the same under the two different excitation wavelengths (λ_{ex} = 294 nm and 366 nm) due to both the two excitation bands as arising from intrinsic defect. However, in the excitation spectrum of Dy^{3+} doped $Ca_4Y_6O(SiO_4)_6$, the excitation bands originating from the host lattice disappears, the sharp peaks due to Dy^{3+} f-f transitions are observed. The peaks located at 291, 320, 346, 360, 385, 420, 450 and 468 nm corresponds to the transitions from the ground state $^6H_{15/2}$ to $^4F_{5/2}$, $^6P_{3/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4K_{17/2}/^4M_{19/2}/^4M_{21/2}$, $^4G_{11/2}$, $^4I_{15/2}$, and $^4F_{9/2}$, respectively. Especially, as can be seen from the Fig. 2, $Ca_4Y_6O(SiO_4)_6$:Dy^{3+} phosphors can be excited by ultraviolet light, NUV light and blue light. The strongest excitation band (peaked at 346 nm) matches well with the NUV LED chips, indicating the potential application for NUV WLEDs.

The emission spectra of $Ca_4Y_6O(SiO_4)_6$:Dy^{3+} phosphors with various concentrations of Dy^{3+} ions excited at the strongest excitation