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A single-phased white-emitting $Ca_2Ga_2GeO_7:Dy^{3+}$ phosphor with different charge compensation ions

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Abstract: A novel white-emitting $Ca_2Ga_2GeO_7:Dy^{3+}$ phosphor was synthesized via a high-temperature solid-state reaction. The crystal phase was analyzed by X-ray diffraction (XRD), and the photoluminescence (PL) properties were studied by luminescence spectra and fluorescence decay curves. Under the excitation of 347 nm, the obtained phosphor exhibited strong emission in the blue region peaked at 478 nm, yellow at 574 nm and a weak red emission band at 665 nm, corresponding to the characteristic transitions of $^4F_{9/2}$ to $^6H_{15/2}$,$^6H_{13/2}$ and $^6H_{11/2}$ of Dy^{3+}, respectively. By varying the doping concentration of Dy^{3+}, tunable colors from blue-white to yellow-white were obtained in the phosphors. Besides, by codoping charge compensators (Li^+, Na^+, K^+ and Ga^{3+}) in $Ca_2Ga_2GeO_7:Dy^{3+}$, the optimum CIE color coordinate and PL intensity were obtained in $Ca_2Ga_2GeO_7:Dy^{3+},K^+$. Accordingly, the PL mechanism of $Ca_2Ga_2GeO_7:Dy^{3+}$ was discussed briefly.

Keywords: phosphor; luminescence; crystal structure; defects; rare earths

Phosphor-converted white light-emitting diodes (pc-WLEDs), which are regarded as the next generation of light sources, have attracted significant attention for use in the lighting industry and in display systems because of their unique properties, including but not limited to high luminous efficiency, energy savings, reliability, small volume, and environment-friendliness[1−5]. At present, the combination of $Y_3Al_5O_{12}:Ce^{3+}$ (YAG:Ce) phosphor with blue InGaN chip is most frequently used[6,7]. Unfortunately, this method suffers the problems of poor color rendering index (R_a<80) and high correlated color temperature (T_c>4500 K), restricting their application[8,9]. To solve the problems mentioned above, the near-UV white light-emitting diodes (NUVLEDs) coupled with red, green and blue trichromatic phosphors are employed, which attract much attention during the past few years[10,11]. This type of white LEDs has a high color rendering index (R_a>90) but low luminous efficiency due to the reabsorption among phosphors[12,13]. In addition, the different degradation rates of the three-primary phosphors will cause color aberration, which is undesirable in practice[14,15]. In these regards, a single-phased white-emitting phosphor pumped by NUVLEDs should be a good choice for phosphor-converted WLEDs, since they exhibit definite advantages, such as improved color stability, better reproducibility, and a simplified fabrication process[16].

Dy^{3+} receives considerable attention in the field of single-phased white-emitting phosphors because of it's dominant emission bands at blue ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) and yellow ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) emission regions of visible spectra. The blue emission hardly varies with the crystal field symmetry around the Dy^{3+} ion[17,18]. The yellow emission, however, being a hypersensitive transition, is strongly influenced by the crystal-field environment. Accordingly, white light could be obtained with appropriate ratio of blue/yellow intensity in some special host lattices[19]. As an important family of luminescent materials, germanates have attracted much attention for the use of the phosphors emitting layer of LEDs due to their high stability and reasonable conductivity as an oxide host[20–22]. $Ca_2Ga_2GeO_7$ host has been reported in more recent study[23], which could be a suitable host for the application in WLEDs when doped with Dy^{3+}.

In this paper, a single-phased white light emitting phosphor $Ca_2Ga_2GeO_7:Dy^{3+}$ was synthesized via a high-temperature solid-state method for the first time. The photoluminescence (PL) properties were investigated as potential candidate to be used in WLEDs. Moreover, the charge compensators (Li^+, Na^+, K^+, Ga^{3+}) were added in $Ca_2Ga_2GeO_7:Dy^{3+}$ phosphor and the effects of which on the PL properties were studied.

1 Experimental

A series of $Ca_{2-x}Ga_2GeO_7:xDy^{3+}$ (x=0.01, 0.02, 0.03,

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0.05, 0.07 and 0.09) phosphors were synthesized by a traditional high-temperature solid-state reaction. $CaCO_3$ (99.99%), Ga_2O_3 (99.99%), GeO_2 (99.99%) and Dy_2O_3 (99.99%) were employed as starting materials. The mixtures were first mixed and ground in an agate mortar for 30 min, and then sintered in air at 1100 ºC for 5.5 h. The as prepared phosphors were cooled to the room temperature and reground for further researches. The Li^+, Na^+, K^+ and Ga^{3+} ions co-doped samples were prepared in the same way except for adding additional stoichiometry amounts of Li_2CO_3 (99.99%), Na_2CO_3 (99.99%), and K_2CO_3 (99.99%) and Ga_2O_3 (99.99%). The phases of the obtained samples were identified by X-ray powder diffraction (XRD) with Cu Kα (λ=0.15418 nm) radiation at a scanning step of 0.02º in the 2θ range from 10º to 80º operating at 36 kV and 30 mA (Rigaku Model D/max-2200). The photoluminescence excitation (PLE) and PL spectra were recorded using a Hitachi F-7000 fluorescence spectrophotometer with a photomultiplier tube operating at 400 V, and a 150-W Xe lamp was used as the excitation lamp. Photoluminescence quantum efficiency was measured by an FLS-920T fluorescence spectrophotometer equipped with a 450 W xenon light source (λ_{ex}=347 nm, λ_{em}=574 nm). The PL decay curves were measured by an FLS980 fluorescence spectrophotometer.

2 Results and discussion

The XRD patterns of $Ca_{1.97}Ga_2GeO_7$:0.03Dy^{3+}, $Ca_{1.91}Ga_2GeO_7$:0.09Dy^{3+}, $Ca_{1.94}Ga_2GeO_7$:0.03Dy^{3+}, 0.03R^+ (R=Li, Na, K) and $Ca_{1.97}Ga_{2.03}Ge_{0.97}O_7$:0.03$Dy^{3+}$ are shown in Fig. 1(a). By comparing with JCPDS Card No. 38-1328, which is also plotted in Fig. 1(a), all the observed diffraction peaks can be indexed to the pure phase of $Ca_2Ga_2GeO_7$. No phase transformation or impurity is observed in the current range of doping concentration. Fig. 1(b) shows the crystal structure of $Ca_2Ga_2GeO_7$ which belongs to the tetragonal with space group $P\bar{4}21m(113)$. There are one Ca^{2+} site (surrounded by six O^{2-} ions), two Ga^{3+} sites (surrounded by four O^{2-} ions) and one Ge^{4+} site (surrounded by four O^{2-} ions) in the compound $Ca_2Ga_2GeO_7$. Based on the effective ionic radii (r) of cations with different coordination numbers (CN) reported by Shannon[24], we propose that Dy^{3+} (CN=6, r=0.091 nm), Li^+ (CN=6, r=0.076 nm), Na^+ (CN=6, r=0.102 nm) and K^+ (CN=6, r=0.138 nm) will occupy Ca^{2+} (CN=6, r=0.1 nm) sites and Ga^{3+} (CN=4, r=0.047 nm) will occupy Ge^{4+} (CN=4, r=0.039 nm) sites preferably because of their similar ionic radius.

Fig. 2 exhibits the PLE and PL spectra of $Ca_{1.97}Ga_2GeO_7$:0.03Dy^{3+}. Monitored at 574 nm, the PLE spectrum clearly demonstrates that there are some intense and sharp lines between 300 and 430 nm, which are assigned to the *f-f* transitions of Dy^{3+}. The excitation peaks are located at 324, 347, 362, 386, and 426 nm, corresponding to the transitions from the ground state $^6H_{15/2}$ to $^6P_{3/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4I_{13/2}$ and $^4G_{11/2}$, respectively[25]. Besides, Ga^{3+}–O^{2-} transition band peaked at 285 nm can also be observed in the PLE spectrum[26]. Under the excitation of 347 nm, the PL spectrum exhibits strong emission in the blue region peaked at 478 nm, yellow at 574 nm and a weak red emission band peaking at 665 nm, corresponding to the characteristic transitions of $^4F_{9/2}$ to $^6H_{15/2}$, $^6H_{13/2}$ and $^6H_{11/2}$ of Dy^{3+}, respectively. Besides, the peak at about 488 nm maybe result from the splitting of energy level for Dy^{3+} in the transitions of $^4F_{9/2}$ to $^6H_{15/2}$.

Fig. 3(a) shows the PL spectra of $Ca_{2-x}Ga_2GeO_7$:$x$$Dy^{3+}$

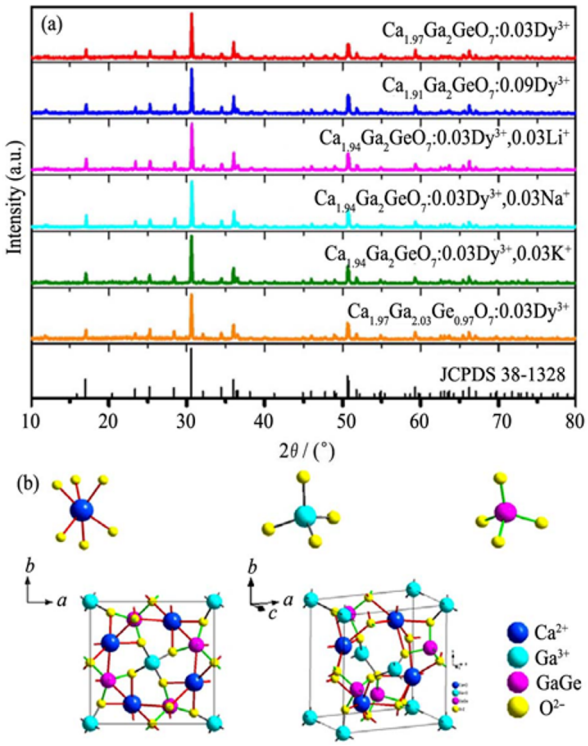

Fig. 1 XRD patterns of $Ca_{1.97}Ga_2GeO_7$:0.03Dy^{3+}, $Ca_{1.91}Ga_2GeO_7$:0.09Dy^{3+}, $Ca_{1.94}Ga_2GeO_7$:0.03Dy^{3+},0.03R^+ (R=Li, Na, K), $Ca_{1.97}Ga_{2.03}Ge_{0.97}O_7$:0.03$Dy^{3+}$ and the standard pattern (JCPDS 38-1328) of $Ca_2Ga_2GeO_7$ (a); Crystal structures of $Ca_2Ga_2GeO_7$ (b)

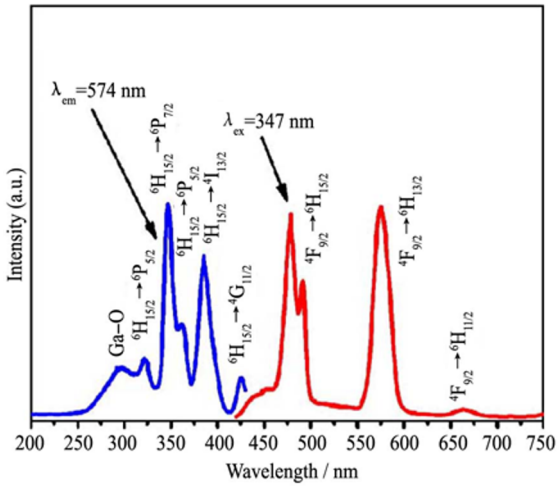

Fig. 2 PLE and PL spectra of $Ca_{1.97}Ga_2GeO_7$:0.03Dy^{3+}