Optical Materials 79 (2018) 247–254

Contents lists available at ScienceDirect

Optical Materials

journal homepage: www.elsevier.com/locate/optmat

# $Eu^{3+}$ doped self-activated $Ca_8ZrMg(PO_4)_6(SiO_4)$ phosphor with tunable luminescence properties

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ARTICLE INFO

*Keywords:*
Phosphor
Self-activated
Energy transfer

ABSTRACT:

Single-host white-light emission phosphors stand a good chance to serve in the next-generation high-power white light emitting diodes. $Eu^{3+}$-doped self-activated $Ca_8ZrMg(PO_4)_6(SiO_4)$ phosphor was synthesized by a high temperature solid-state reaction which can realize white light emission by tuning spectrum. The analysis of XRD, SEM, UV–vis DRS, luminescent spectra, and emission dynamic curves were applied to investigate the obtained samples. Upon 295 nm excitation, the $Ca_8ZrMg(PO_4)_6(SiO_4)$: $Eu^{3+}$ phosphors contain two dominating bands peaked at 470 and 615 nm, which are attributed to the charge transfer (CT) transition from $Zr^{4+}$ to $O^{2-}$ and the characteristic transition $^5D_0 \rightarrow {}^7F_2$ of the $Eu^{3+}$ ions, respectively. In view of the energy transfer between Zr-O CT and $Eu^{3+}$ ions, the chromaticity coordinates of $Ca_8ZrMg(PO_4)_6(SiO_4)$: $Eu^{3+}$ phosphors can be tuned from (0.2186, 0.2858) to (0.5413, 0.3295). Present work indicates that the novel $Ca_8ZrMg(PO_4)_6(SiO_4)$ is a promising candidate as a single-host white phosphor with an excellent thermal stability for optical display applications.

## 1. Introduction

The phosphors with white-light emission have attracted much attention for their applications in optical display fields. The white-light emission can be generated in single-host phosphors through single-doping a type of activator or co-doping with sensitizer and activator *via* energy transfer processes [1], for examples, $Zn_2SiO_4$: $RE^{3+}$ (Eu, Dy, Sm) [2], $Ca_{19}Ce(PO_4)_{14}$: $Tb^{3+}$, $Mn^{2+}$ [3], $Ca_9Lu(PO_4)_7$: $Eu^{2+}$, $Mn^{2+}$ [4], $LiYSiO_4$:$Ce^{3+}$, $Tb^{3+}$, $Eu^{3+}$ [5], and so on. As a consequence, a single-host white-emitting phosphor is considered to be potentially useful because of small color aberration, high color rendering, and low cost [6].

In recent years, the broad UV–visible emissions have been reported in single-host phosphors with tetravalent ($M^{4+}$) cations, such as $Zr^{4+}$, $Ce^{4+}$, and $Ti^{4+}$ in which the $M^{4+}$-$O^{2-}$ charge transfer (M − O CT) transition is responsible for the emissions [7-12]. The M − O CT transition takes place uniquely from the $M^{4+}$ ions with octahedral coordination of oxygen ions [1]. The luminescence properties and their applications of the $Zr^{4+}$-containing phosphors have already been studied due to the fact that the excitation bands of the $Zr^{4+}$-$O^{2-}$ groups are usually located at very short wavelength region [13], for instance, $CaZr(PO_4)_2$, $Ca_2ZrSi_4O_{12}$, and $ZrSiO_4$ show the emission in the wavelength region 280–380 nm under excitation by the UV-VUV light (130–250 nm) [11] or the X-ray excitation [14]. And the $Zr^{4+}$ emissions in the visible region have been reported in a few phosphors, such as $K_2YZr(PO_4)_3$ [1], $Ca_4ZrGe_3O_{12}$ [8] and $Ca_3ZrSi_2O_9$ [9]. Furthermore, the phosphors with $Zr^{4+}$ ions can accommodate various activators. Usually heavy metal ions such as $Zr^{4+}$ in hosts have great influence on nonlinear optics, dielectrics, ferroelectric, valence states of activators [13]. The white-light emission is realized in single-host $K_2EuZr(PO_4)_3$ by combining the $Zr^{4+}$-emission (greenish-blue) with the $Eu^{3+}$ ions emission (red) [1]. Luminescent properties of $Ca_{1-x}Mn_xZr(PO_4)_2$ phosphors can be tuned by changing $Mn^{2+}$ content, and the green emission had saturated at $x = 0.07$ [11].

In this study, we report the $Zr^{4+}$-emission in the visible luminescence and the tunable white-light emission which is realized in $Ca_{8-x}ZrMg(PO_4)_6(SiO_4)$: $xEu^{3+}$ under UV excitation at room temperature. Additionally, the crystal structure, excitation and emission spectra, decay curves and energy transfer mechanism are investigated and discussed in detail.

## 2. Experimental

The $Ca_8ZrMg(PO_4)_6(SiO_4)$ host and a series of $Eu^{3+}$ doped $Ca_8ZrMg(PO_4)_6(SiO_4)$ phosphors were prepared by high temperature solid-state reaction method under air atmosphere. The raw materials were $CaCO_3$

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https://doi.org/10.1016/j.optmat.2018.03.055
Received 8 February 2018; Received in revised form 19 March 2018; Accepted 27 March 2018

(99.9%, Aladdin), $ZrO_2$ (99.9%, Aladdin), $MgCO_3$ (99.9%, Aladdin), $SiO_2$ (99.9%, Aladdin) $NH_4H_2PO_4$ (99.9%, Aladdin) and $Eu_2O_3$ (99.99%). Stoichiometric amounts of staring materials were thoroughly mixed in an agate mortar by grinding and sintered at 1400 °C in air atmosphere for 2 h. The heating rate was controlled at 6–7 °C/min. Finally, after cooling to room temperature, all of the as-synthesized samples were ground into powders and collected for further measurements.

The X-ray diffraction (XRD) data were collected on an X-ray diffraction (Bruker Axs D2 PHASER diffractometer) using Cu Kα radiation (λ = 1.5405 Å) in the 2θ ranging from 10° to 80°. The morphology and elemental analysis were characterized by scanning electronic microscopy (SEM). The interplanar crystal spacing was carried out by transmission electron microscope (TEM, HitachiH-9500). The diffuse reflectance spectra were analyzed with a Shimadzu UV-3600 UV–Vis spectrometer. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were examined by a PL3-211-P spectrometer (HORIBA JOBIN YVON, America) and a 450 W xenon lamp was used as the excitation source. The luminescence decay curves were measured using a nano LED (280 nm) and a spectral LED (460 nm) of pulsed Nd: YAG lasers, respectively.

## 3. Results and discussion

### 3.1. Crystal structure

The typical powder XRD patterns of $Ca_{8-x}ZrMg(PO_4)_6(SiO_4)$: $xEu^{3+}$ ($x$ = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7) and the Inorganic Crystal Structure Database (ICSD) Card file (No. 85090) of $Ca_8CeMg(PO_4)_6(SiO_4)$ as a reference are shown in Fig. 1(a). In fact, there is no standard data of $Ca_8ZrMg(PO_4)_6(SiO_4)$ reported in the database of JCPDF. But from Fig.1 (a), it is clearly found that all the diffraction peaks of $Ca_8ZrMg(PO_4)_6(SiO_4)$ can be well indexed to the standard data of $Ca_8CeMg(PO_4)_6(SiO_4)$, indicating that the structures between them are extremely similar. Therefore, the ICDS Card file of $Ca_8CeMg(PO_4)_6(SiO_4)$ can been taken to characterize the phase purity of the samples. In addition, with the $Eu^{3+}$ ions concentration increasing, the peak positions of the diffraction patterns shift toward larger angle due to the substitution of the smaller $Eu^{3+}$ for the larger $Ca^{2+}$.

To further investigate the structure of the obtained samples, Rietveld refinement of $Ca_{7.4}ZrMg(PO_4)_6(SiO_4)$: $0.6Eu^{3+}$ performed with the experimental powder diffraction data are shown in Fig. 1(b). In addition, the corresponding refined parameters are listed in Table 1. The result of the Rietveld refinement reveals that the $Ca_{7.4}ZrMg(PO_4)_6(SiO_4)$:$0.6Eu^{3+}$ crystallizes in a trigonal unit cell with space-group R3c(161), $a = b = 10.49$ Å, $c = 37.53$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 3577.70$ Å$^3$, $Z = 6$. And the refinement finally converges to $R_{wp} = 9.42\%$, $R_p = 6.7\%$ and GOF = 2.10. Fig. 1(c) displays the schematic structure of $Ca_8ZrMg(PO_4)_6(SiO_4)$ and the coordinated condition of Ca1Zr1Mg1(18b), Ca2Zr2(18b), Mg2Zr3(6a) and PSi(6a), which are 5, 5, 6, and 4-coordinated, respectively.

Furthermore, the elements (O, Mg, Si, P, Ca, Zr and Eu) in the phosphor are presented in the energy dispersive spectrum of $Ca_{7.4}ZrMg(PO_4)_6(SiO_4)$: $0.6Eu^{3+}$ (Fig. 2(a)), which indicates the doped $Eu^{3+}$ ions are confirmed to be uniformly distributed in the host. Besides, the SEM and TEM images of $Ca_8ZrMg(PO_4)_6(SiO_4)$ host were displayed in Fig. 2 (b) and (c), respectively. The SEM image clearly shows the slightly aggregated particles with a size about 0.5 μm. And the crystal lattice stripe and figure of electron diffraction FFT are shown in Fig. 2 (d) and (e), which reveals the interplanar crystal spacing is 0.406 nm, corresponding to the crystal face (0, 2, 4).

### 3.2. Diffuse reflection spectra

The diffuse reflection spectra of $Ca_8ZrMg(PO_4)_6(SiO_4)$ host and $Eu^{3+}$-doped $Ca_8ZrMg(PO_4)_6(SiO_4)$ phosphors are illustrated in Fig. 3.

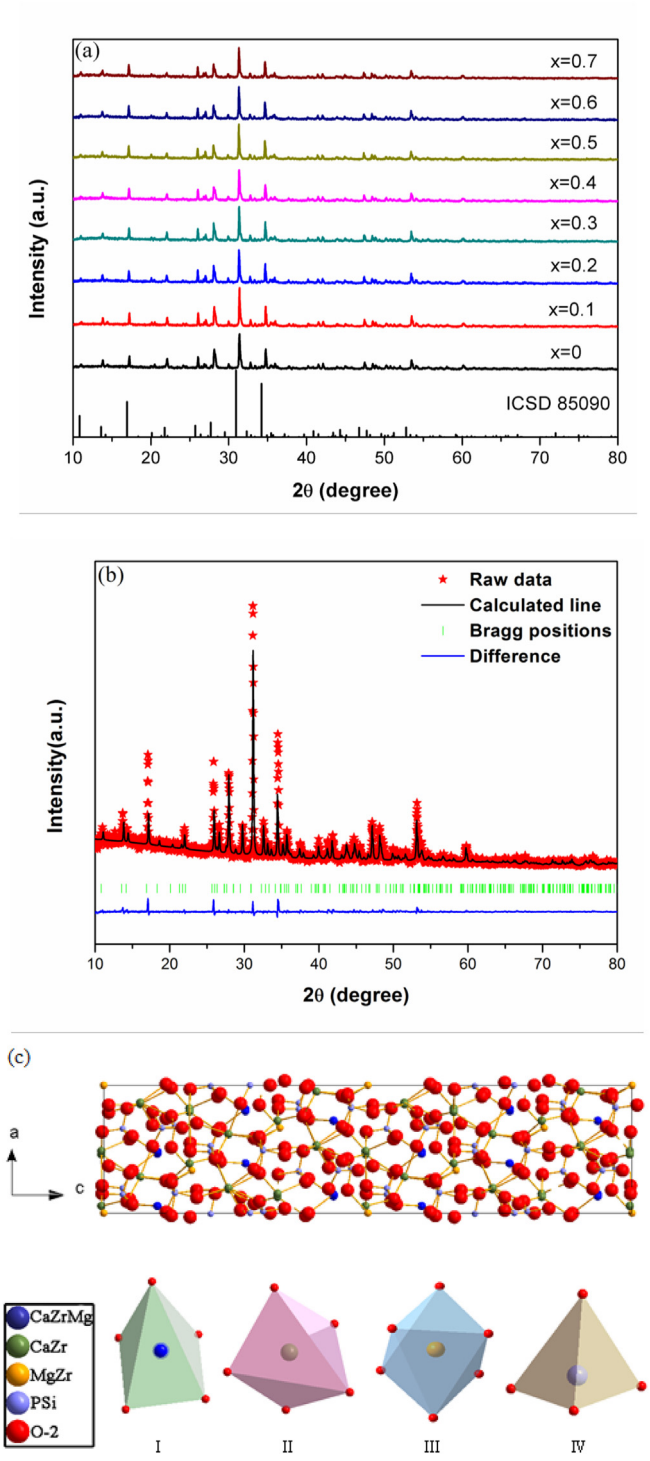


**Fig.1.** (a) XRD patterns of $Ca_{8-x}ZrMg(PO_4)_6(SiO_4)$: $xEu^{3+}$ ($x$ = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7), and the standard data for $Ca_8CeMg(PO_4)_6(SiO_4)$ (ICSD card No.85090) is shown as comparison; (b) Rietveld refinement of the powder XRD pattern of $Ca_{7.4}ZrMg(PO_4)_6(SiO_4)$: $0.6Eu^{3+}$ sample; (c) Schematic structure of $Ca_8ZrMg(PO_4)_6(SiO_4)$, (I, II, III and IV were the coordination environment of CaZrMg, CaZr, MgZr and PSi sites in $Ca_8ZrMg(PO_4)_6(SiO_4)$, respectively.).

The $Ca_8ZrMg(PO_4)_6(SiO_4)$ host shows high reflection in the range of 380–800 nm and exhibits obvious energy absorption from 230 to 250 nm and 250–380 nm, corresponding to the absorption of host lattice or oxo-anion group, -$PO_4$, -$SiO_4$ and the CT of $O^{2-}\rightarrow Zr^{4+}$, respectively [15]. With the increase of $Eu^{3+}$ ions doping into $Ca_8ZrMg$