Photoluminescence of Eu^{3+}-doped triple phosphate Ca$_8$MgR(PO$_4$)$_7$ (R = La, Gd, Y)

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ABSTRACT

Eu^{3+}-doped triple phosphate Ca$_8$MgR(PO$_4$)$_7$ (R = La, Gd, Y) was synthesized by the general high-temperature solid-state reaction. Excitation and emission spectra as well as luminescence decay were used to characterize the phosphors. Photoluminescence excitation and emission spectra showed that the phosphor could be efficiently excited by UV–vis light from 260 to 450 nm to give bright red emission assigned to the transition (^{5}D$_0$→^{7}F$_2$) at 612 nm. The richness of the red color has been verified by determining their color coordinates (X, Y) from the CIE standard.

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1. Introduction

Orthophosphates with the tetrahedral rigid three-dimensional matrix have been paid intense attention because of their excellent properties, e.g., the large band gap and the high absorption of PO$_4^{3-}$ in VUV region, moderate phonon energy, the high chemical stability, and the exceptional optical damage threshold [1–3]. Phosphate compounds are important luminescence hosts, which can produce plenty of crystal field environments imposed on emission centers. Phosphate-based phosphors activated with Eu^{3+} ions have been paid much attention [4–6]. And rare earth (RE) ions doped monophosphates have excellent thermal stability [1,7–9]. For example, Tang et al. confirmed that KSrPO$_4$ doped with Eu^{2+} prepared by solid-state reaction show higher thermally stable luminescence which was found to be better than commercially available Y$_3$Al$_5$O$_{12}$:Ce^{3+} phosphor [7].

Calcium phosphate Ca$_3$(PO$_4$)$_2$ and its variations are important phosphates that have been extensively studied. It has been investigated that calcium phosphate usually exists in two stable forms α- and β-modifications. α-Ca$_3$(PO$_4$)$_2$ (space group P21/a, Z = 24) has a distorted β-K$_2$SO$_4$-type structure. Calcium cations fully occupy the 18 (four-fold) positions [10].

β-Ca$_3$(PO$_4$)$_2$ (space group R3c, Z = 21) is iso-structural to the natural mineral whitlockite: Ca$_{18.19}$Mg$_{1.17}$H$_{1.62}$(PO$_4$)$_{14}$. In β-Ca$_3$(PO$_4$)$_2$ crystal structure, Ca^{2+} ions are distributed between five crystallographic sites. Four of them Ca(1), Ca(2), Ca(3) and Ca(5) are completely filled, the Ca(4) site is only half occupied. The Ca(1), Ca(2) are seven and Ca(3) eight coordinated to oxygen atoms. Ca(4) is six coordinated, similar to Ca(5), whose environment is nearly octahedral, however, with only a small axial (trigonal) distortion component [11,12]. The stability of a structure with half-occupied Ca(4) position makes it possible to assume the existence of a crystal structure where this position is fully occupied or completely empty. This special crystal structure permits the rich heterovalent substitution by the mechanism to occupy or to form vacancies in the structure [11], for example, 3Ca^{2+}→2R^{3+}+□ (R^{3+} = RE, Y, Fe, Al) gives the formation of the cationic vacancies in solid solutions of Ca$_{3-x}$R$_{2x/3}$(PO$_4$)$_2$ (0⩽x⩽3/7); and 3Ca^{2+}+□→R^{3+}+3M$^+$ or Ca^{2+}+□→2M$^+$ (M = Li, Na, K) gives the occupation of cationic vacancies in the solid solutions of Ca$_{3-x}$Na$_x$R$_{x/3}$(PO$_4$)$_2$ (0⩽x⩽3/7) or Ca$_{3-x}$M$_{2x}$(PO$_4$)$_2$ (0⩽x⩽1/7) [11]. The substitutions of calcium in β-Ca$_3$(PO$_4$)$_2$ by

metals ions have been investigated [13–15]. These materials, which preserve a polar whitlockite-type crystal structure, have served as the base for the crystallochemical design of compounds with ferroelectric, nonlinear-optical, and ion-conductive properties [16,17]. Among these compounds there are phosphors, catalysts, sensor materials, and materials for two-stage hydrogen oxidation [12,18–20]. Teterskii et al. [16] have investigated dielectric and second harmonic generation (SHG) tests for the whitlockite solid solutions $Ca_{9-x}M_xR(PO_4)_7$ ($x = 1$, 1.5; M = Mg, Zn, Cd; R = Ln, Y) [16]. However, luminescence of this kind of phosphate was rarely reported.

In this study, Eu^{3+}-doped triple phosphate phosphors, $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y), were synthesized by the conventional high-temperature solid-state reaction. Photoluminescence excitation and emission spectra, the decay properties of Eu^{3+} ions and their color coordinates (X, Y) in this Eu^{3+}-doped phosphor were investigated.

2. Experiments

Polycrystalline samples of Eu^{3+}-doped $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y) were synthesized using a conventional solid-state reaction. The starting material was a stoichiometric mixture of reagent grade $C_4Mg_4O_2$–$H_2MgO_2 \cdot 5H_2O$, $CaCO_3$, $(NH_4)_2HPO_4$, and rare earth oxides (La_2O_3, Gd_2O_3, Eu_2O_3) and Y_2O_3. Firstly, the mixture was heated up to 350 °C and kept at this temperature for 10 h. The obtained powder was thoroughly mixed in acetone and then heated up to 750 °C and kept at this temperature for 5 h in air. After that, the sample was thoroughly mixed and heated in air at 1100 and 1300 °C for 10 h, respectively. The Eu^{3+}-doped samples were prepared with the doping concentrations of 5.0 mol% of R^{3+}. XRD patterns of Eu^{3+}-doped $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y) phosphors are nearly the same with the JCPDS Card No. 70-2065. No impurity lines were observed, and all the reflections could be well indexed to whitlockite-type hexagonal structure of β-$Ca_3(PO_4)_2$ with $R3c$ space group [21].

Photoluminescence excitation spectra and UV-excited luminescence spectra were recorded on a Perkin-Elmer LS-50B luminescence spectrometer with Monk–Gillieson type monochromators and a xenon discharge lamp used as excitation source. All the measurements were performed at room temperature (RT). The fluorescence decay curve for the emission $^5D_0$–$^7F_2$ was measured under excitation of 266 nm pulsed YAG laser at RT.

3. Results and discussion

Fig. 1 presents the emission spectra of $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y) compounds excited by 254 nm commercial lamp. There are groups of sharp lines assigned to the transitions of $^5D_0$–^7F_J ($J = 0$, 1, 2, 3, 4) levels of Eu^{3+}. The emission at about 580 nm is the transition $^5D_0$–$^7F_0$. The emission around 590 nm originates from the magnetic dipole transition $^5D_0$–$^7F_1$. The dominated red emission of 612 nm is attributed to the electric dipole transition $^5D_0$–$^7F_2$, indicating that Eu^{3+} is located at the site of non-inversion symmetry [22]. The emission corresponding to the transition of $^5D_0$–$^7F_{3,4}$ are too weak, so they are not presented on the figure.

The excitation spectra by monitoring $^5D_0 \rightarrow {}^7F_2$ emission of Eu^{3+} in $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y) compounds are shown in Fig. 2. It can be divided into two regions: the broad excitation band in 220–300 nm region originates from the charge transfer transition of the Eu^{3+}–O^{2-} bond (CTB) [22]. The other sharp lines can be assigned respectively to the transitions between the ground level $^7F_0$ and the excited levels ^5H_J, $^5D_4$, ^5G_J, $^5L_6$, $^5D_{3,2,1}$ [23]. Usually, in Eu^{3+}-doped phosphors, the intensity of CTB is much more intense
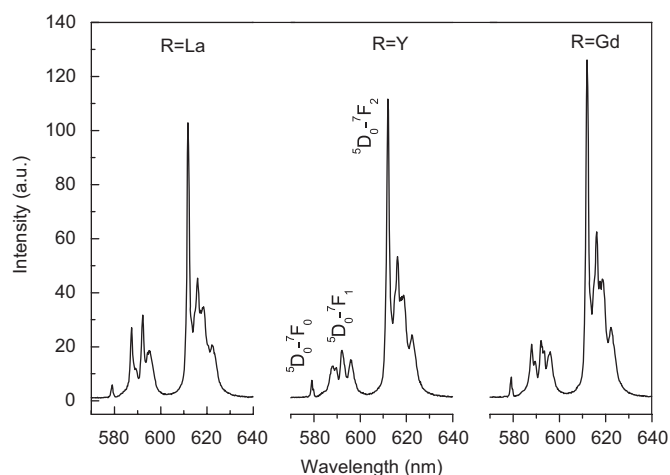

Fig. 1. The RT luminescence spectra of $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y) under 254 nm excitation using lamp source.
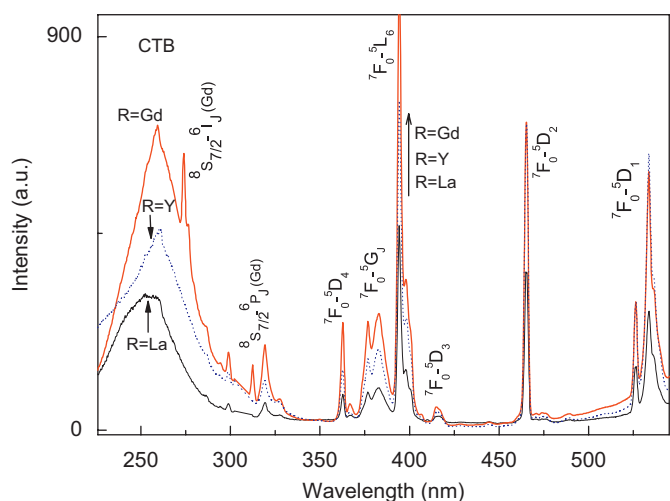
Fig. 2. The excitation spectra of $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y) by monitoring 612 nm.

than that of f–f transitions in the excitation spectrum. For the as prepared samples, the intensities of f–f absorption transitions are higher than that of CTB. This phenomenon is also observed in some of other phosphors, such as α-$Gd_2(MoO_4)_3$ and $NaM(WO_4)_{2-x}(MoO_4)_x$:Eu^{3+} (M = Gd, Y, Bi) [24,25]. Up to now, there is no reasonable explanation for this experimental phenomenon. Probably, this abnormal properties is due to the nature of $Ca_8MgR(PO_4)_7$ structure and sites of Eu^{3+} occupied in the matrix. In the excitation of $Ca_8MgGd(PO_4)_7$:Eu^{3+}, the sharp peak at 274 nm superimposed on Eu^{3+} CTB is due to a $^8S_{7/2}$–^6I_J transition Gd^{3+} in the host lattice [22].

Under the excitation of CTB at 254 nm, as can be seen that the red emission lines at 612 nm originating from the electric dipole transition $^5D_0$–$^7F_2$ is the dominant luminescence in the spectrum in Fig. 1. The crystal splitting components of $^5D_0$–$^7F_1$ and $^5D_0$–$^7F_2$ of Eu^{3+} can be observed, but not totally resolved due to the weak experimental resolution.

In general, when the Eu^{3+} ion is located at the crystallographic site without inversion symmetry, its hypersensitive transition $^5D_0$–$^7F_2$ red emission will dominate in the emission spectrum [22]. The spectral properties of Eu^{3+} in $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y) are in good agreement with the crystal structure. The whitlockite-like solid states have no inversion center; as a result,
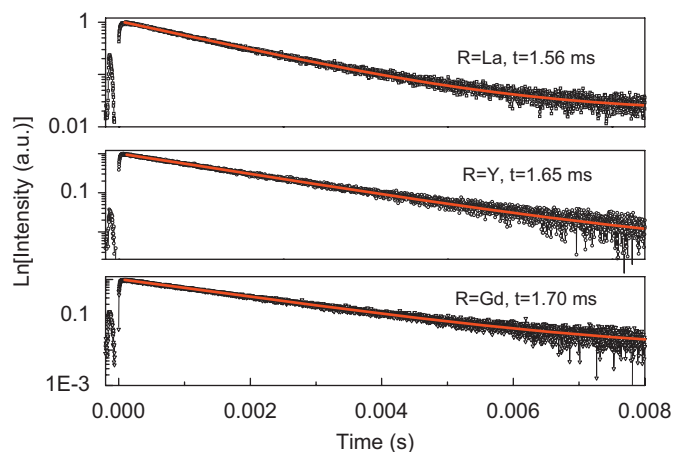
Fig. 3. The luminescence decay curve of 612 nm emission in $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y) under the excitation of 266 nm pulsed YAG laser.

Table 1
Color coordinates (X, Y) of Eu^{3+}-doped $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y) phosphors in this work and compared with the references of Eu^{3+}-doped La_2O_2S, Gd_2O_2S and Y_2O_2S phosphors [28]

Powder phosphor	X	Y
$Ca_8MgLa(PO_4)_7$	0.643	0.356
$Ca_8MgGd(PO_4)_7$	0.649	0.351
$Ca_8MgY(PO_4)$	0.650	0.350
$La_2O_2S:Eu^{3+}$	0.641	0.358
$Gd_2O_2S:Eu^{3+}$	0.647	0.352
$Y_2O_2S:Eu^{3+}$	0.665	0.334

the SHG effect exists in them [16]. In $Ca_8MgR(PO_4)_7:Eu^{3+}$ (R = La, Gd, Y), the Eu^{3+} will replace the R^{3+} in view of their similar sizes and valence state. So the Eu^{3+} is located at a site without inversion center. Consequently, $^5D_0$–$^7F_2$ red emission (612 nm) presents the most prominent intensity in all the three emission spectra (Fig. 1).

The fluorescence decay curves for the $^5D_0$ level at 612 nm emission ($^5D_0$–$^7F_2$) under excitation of 266 nm pulsed YAG laser are shown in Fig. 3. The curve can be fitted into a single exponential function as: $I = I_0 \exp[-t/\tau]$, I_0 is the initial emission intensity for $t = 0$, τ is lifetime. The lifetime of Eu^{3+} in $Ca_8MgR(PO_4)_7:Eu^{3+}$ (R = La, Gd, Y) are calculated to be 1.56, 1.65, and 1.70 ms for R = La, Y and Gd, respectively.

It is found that both the emission intensity and lifetime of Eu^{3+} decrease in the sequence of R = Gd > Y > La. $Ca_8MgGd(PO_4)_7:Eu^{3+}$ presents the highest emission intensity and lifetimes. This can be due to the energy transfer from Gd^{3+} to Eu^{3+} ions. On the excitation spectra of $Ca_8MgGd(PO_4)_7:Eu^{3+}$ (Fig. 2), the excitation lines of Gd^{3+} (274 nm for $^8S_{7/2}$–^6I_J and 312 nm for $^8S_{7/2}$–^6P_J) can be observed, indicating that the energy transfer can occur from Gd^{3+} to Eu^{3+}. On excitation into the CTB of Eu^{3+}, the excitation energy can relax directly from these excited states to the $4f$ levels of Eu^{3+} ions. On the other hand, excitation energy can also transfer to the $4f$ levels of Eu^{3+} via the Gd^{3+}-sublattice to produce the emission. This transfer process cannot occur in $Ca_8MgLa(PO_4)_7$ and $Ca_8MgY(PO_4)_7$. The ionic radii for Eu^{3+}, La^{3+}, and Y^{3+} are 0.947, 0.103 and 0.90 nm (for six coordination), respectively [26]. In Eu^{3+}-doped $Ca_8MgLa(PO_4)_7$ and $Ca_8MgY(PO_4)_7$, the Eu^{3+} ions could have a stiff lattice environment in the $Ca_8MgY(PO_4)_7$, but in a loose one in $Ca_8MgLa(PO_4)_7$. The stiffer the host lattice, the higher the emission intensity of the activator ions [27]. It could be expected that the expansion after excitation is not as strongly restricted by the surrounding of the luminescent ions in $Ca_8MgLa(PO_4)_7$ as in $Ca_8MgY(PO_4)_7$. More nonradiative relaxations take place in $Ca_8MgLa(PO_4)_7$ than in $Ca_8MgY(PO_4)_7$. Consequently, the Eu^{3+} show higher emission intensity and longer lifetimes in $Ca_8MgY(PO_4)_7$ than in $Ca_8MgLa(PO_4)_7$.

Following the standard procedure that has been made available by the CIE (France), we have computed the color coordinates (X, Y), which are given in Table 1, from which it can be seen that the color purity could satisfy the need for red phosphors. These color coordinates are well in agreement with the standard coordinates reported earlier in the literature for certain commercial red phosphors [28].

4. Conclusion

$Ca_8MgR(PO_4)_7:Eu^{3+}$ (R = La, Gd, Y) phosphors were prepared by the solid-state reaction at 1300 °C in air atmosphere. This phosphor can be effectively excited by both C–T band and ultraviolet light 395 nm and blue light 465 nm, and emits strong red light (612 nm), which belongs to the electric dipole transition ($^5D_0 \rightarrow {}^7F_2$) of Eu^{3+} ions. Both the emission intensity and lifetime of Eu^{3+} in $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y) decrease in the sequence of R = Gd > Y > La, which have been explained in accordance with the crystal structures. The CIE results lie within the recommended values of the color coordinates. This experiment indicates that this kind of triple phosphate $Ca_8MgR(PO_4)_7$ (R = La, Gd, Y) may provide another red phosphor choice for the LEDs applications. The further works, for example, the influence of crystallographic sites on luminescence of Eu^{3+} ions in this host should be investigated and in progress.

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