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Synthesis and photoluminescence properties of $MgAl(PO_4)O:Eu^{3+}$ red phosphor for white LEDs

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Abstract

Eu^{3+}-activated $MgAl(PO_4)O$:phosphor has been synthesized by a high temperature solid state reaction and efficient red emission under near-ultraviolet excitation is observed. The emission spectrum shows a dominant peak at 594 nm due to the $^5D_0 \rightarrow {}^7F_1$ transition of Eu^{3+}. The excitation spectrum is coupled well with the emission of UV LED (350–410 nm). The effect of Eu^{3+} concentration on the luminescent properties of $MgAl(PO_4)O:Eu^{3+}$ and the mechanism of concentration quenching of Eu^{3+} are studied. The results show that $MgAl(PO_4)O:Eu^{3+}$ is a promising red-emitting phosphor for white LEDs.

Keywords: Eu^{3+} doped; Luminescent properties; $MgAl(PO_4)O$

1. Introduction

White light-emitting diodes (LEDs) are considered as the next generation light source because of their low electric consumption, environment friendly, high brightness, long lifetime, good reliability, fast response etc. [1–4]. The general strategy of producing white light is to combine a blue LED with a yellow emitting phosphor ($YAG:Ce^{3+}$) [5]. However, such a combination exhibits a poor color rendering index (<80) due to the lack of a red light component [6]. Recently, near-ultraviolet (NUV) InGaN-based LEDs, which range from 350 to 420 nm received more attention because NUV–LED combine a NUV chip with red, green, and blue (RGB) phosphors to generate warm white lights and can offer a highly efficient solid-state lighting [7,8]. However, the luminescent effect of red phosphor is lower than that of the green and blue phosphor at UV excitation region, and the most widely used red phosphor $Y_2O_2S:Eu^{3+}$, is also chemically unstable [9,10]. Thus, researchers are interested in the red phosphor with higher chemical stability that can be excited by NUV light.

Phosphates are excellent matrices for rare earth ions activated phosphors for their easy-synthesis, low-cost and chemical/thermal-stabilities over a wide range of temperatures [400–800 °C] [11]. In this work, we focused on a new type of phosphate phosphor host, $MgAl(PO_4)O$, which is well-known as artificial material as molecular sieve [12], catalytic agent [13,14] and mesoporous material [15]. It exhibits excellent properties as a potential host of phosphor, e.g., the large band gap, the high absorption of $(PO_4)^{3-}$ in the NUV region, and moderate phonon energy [16]. Moreover, as far as we know that there are few reports about rare earth doped $MgAl(PO_4)O$ phosphor for white LED.

We first observed the apparent broadband blue–green luminescence from Eu^{2+} doped $MgAl(PO_4)O$ [17]. In this article, we report on the red emission from $MgAl(PO_4)O:Eu^{3+}$ phosphor, especially the effect of crystals structure on the Eu^{3+}luminescence prosperities and mechanism of

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concentration quench of Eu^{3+} in this Phosphates. It is suggested that $MgAl(PO_4)O{:}Eu^{3+}$ is a potential red-emitting phosphor for white LEDs.

2. Experimental

A series of Eu^{3+} doped $MgAl(PO_4)O$ samples $Mg_{1-x}Al(PO_4)O{:}xEu^{3+}$ ($x=0.005$, 0.010, 0.015, 0.020, 0.025, 0.030, 0.035, 0.040) were prepared by solid-state reactions, $MgCO_3$ (A.R.), $AlPO_4$ (A.R.), and Eu_2O_3 (99.99%) were used as reagents for sample preparation. Raw materials with the stoichiometrical ratio were weighed and ground finely in an agate mortar. Then the mixture was put into corundum crucibles, and heated at 1300 °C for 2 h. Finally, the sample was gained by a fully grinding in an agate mortar after cooling to room temperature naturally in the desired ratio.

The synthesized samples were characterized by X-ray diffraction (XRD) using a D/Max2200 X-ray diffractometer (40 kv and 40 mA, Cu Kα). Fluorescence spectra were measured using a spectrophotometer in the wavelength range of 200 nm to 900 nm (Spectrophotometer F-7000; Hitachi Ltd.). The UV–vis optical absorption spectra in the wavelength range of 200 nm to 700 nm were measured on a HITACHIU-4100 spectrophotometer. All measurements were performed at ambient temperature.

3. Results and discussion

Fig. 1 shows a typical XRD pattern of Eu^{3+} doped $MgAl(PO_4)O$ sample. Most peaks are indexed to the $MgAl(PO_4)O$ phase, which agrees well with JCPDS No. 82-0727. It was found that there is no detectable phase change within the whole range of Eu^{3+} concentration, which indicates that the doping of Eu^{3+} ions does not form a new phase in the synthesis process.

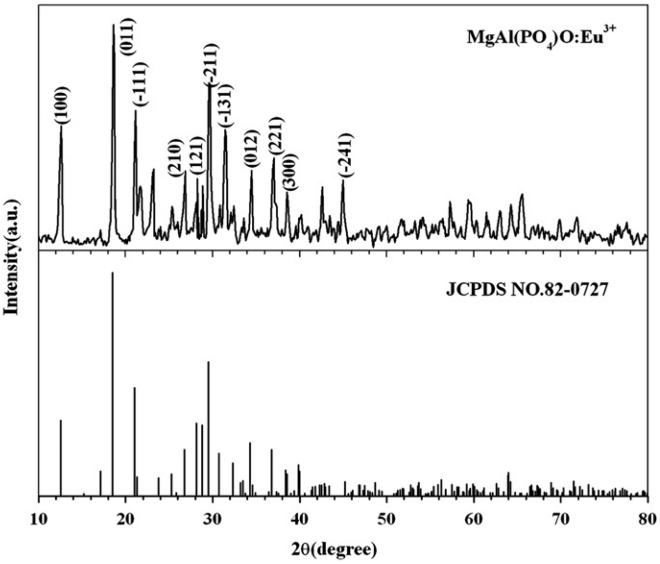

Fig. 1. XRD pattern of Eu^{3+} doped $MgAl(PO_4)O$.

$MgAl(PO_4)O$ has a monoclinic crystal structure with a space group of $P2_{1/c}$ and lattice parameters values $a=7.111$ (2) Å, $b=10.362$ (3) Å, $c=5.455$ (3) Å, $\beta=98.38$ (5), $Z=4$, $V=397.7$ Å [18]. Fig. 2 presents the crystal structures of $MgAl(PO_4)O$. Its structure contains AlO_4 tetrahedron which form single chains with the periodicity of two tetrahedral along the crystallographic *c*-direction. These chains are connected with each other via isolated PO_4 tetrahedron. Mg^{2+} ions occupy a single crystallographic position, which is surrounded by oxygen in the form of a trigonal bipyramid. Two of these polyhedrons are connected via edges to form small clusters. These are linked to four surrounding bipyramids via common corners to form a two-dimensional net. These Mg^{2+} sites are separated from each other in the *b*-direction by the layers formed by the tetrahedral Al_2O_6 chains and the connecting PO_4 tetrahedra [19].

The UV–visible optical absorption spectra of $MgAl(PO_4)O$ and $Mg_{0.965}Al(PO_4)O{:}0.035\ Eu^{3+}$ are shown in Fig. 3. The undoped $MgAl(PO_4)O$ host exhibits the broad absorption band from 230 to 360 nm. The absorption spectrum of the $Mg_{0.965}Al(PO_4)O{:}0.035\ Eu^{3+}$ phosphor consists of two parts. One is a broadband from 220 to 420 nm assigned to the overlap of Eu^{3+}–O^{2-} charge-transfer state (CTS) band and $(PO_4)^{3-}$ group absorption, and the other is sharp peaks in the range from 320 to 600 nm that are associated with typical intra-4f forbidden transition of the Eu^{3+} ions [20].

Fig. 4 presents the typical excitation and emission spectra of $Mg_{0.965}Al(PO_4)O{:}0.035\ Eu^{3+}$. In the excitation spectrum by monitoring $^5D_0$–$^7F_2$ emission of Eu^{3+} (Fig. 4(a)), the broad excitation band peaked at about 260 nm is attributed to the charge transfer band (CTB) resulting from an electron transfer from the ligand O^{2-} (2p) orbital to the empty states of the 4f configuration of Eu^{3+} [21], while the lines in the 350–500 nm range belong to the transitions between the ground level $^7F_0$ and the excited levels $^5D_4$, ^5G_J, $^5L_6$, $^5D_2$, respectively. It is a good property for these phosphors that ultraviolet light (400 nm) can be strongly absorbed, which is nicely in agreement with the near-UV LED chips.

The relative emission spectra of $Mg_{0.965}Al(PO_4)O{:}0.035\ Eu^{3+}$ under the excitation of 400 nm are shown in Fig. 4(b). The spectra consist of a number of sharp lines ranging from 570 to 710 nm, which are associated with the transitions from the excited state $^5D_0$ to ^7F_J ($J=0$, 1, 2, 3 and 4) levels of Eu^{3+}. It is well-known that the $^5D_0 \rightarrow {}^7F_1$ transition belongs to the magnetic dipole transition which scarcely changes the crystal field strength around the Eu^{3+} ions, and this transition is independent of the symmetry and the site occupied by Eu^{3+} ions in the host electric dipole transition. While the transition of $^5D_0 \rightarrow {}^7F_2$ belongs to a forced electric dipole transition and its intensity is very sensitive to the site symmetry of the Eu^{3+} ions [22]. If Eu^{3+} ions occupy an inversion symmetry site, the o-red emission, magnetic transition $^5D_0$–$^7F_1$ is the dominant transition; on the contrary, the electric dipole transition

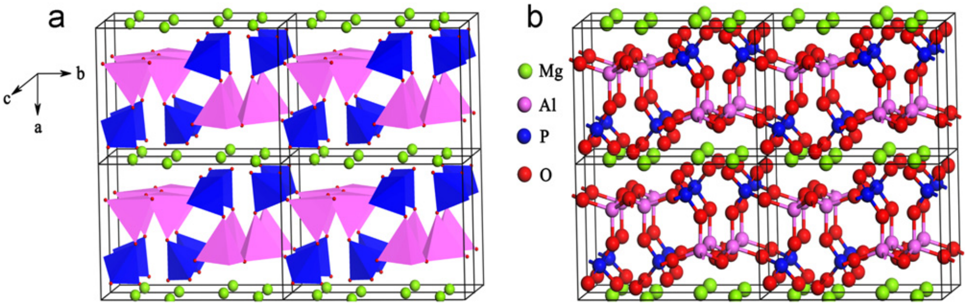

Fig. 2. Crystal structure of $MgAl(PO_4)O$.

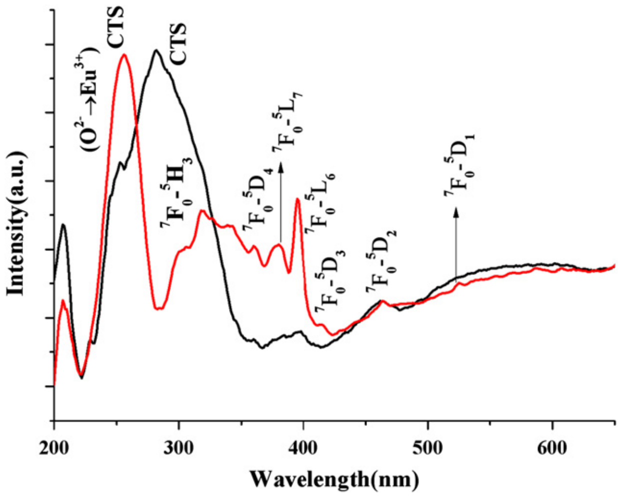

Fig. 3. UV–vis optical absorption spectra of $Mg_{0.965}Al(PO_4)O$:0.035 Eu^{3+}.

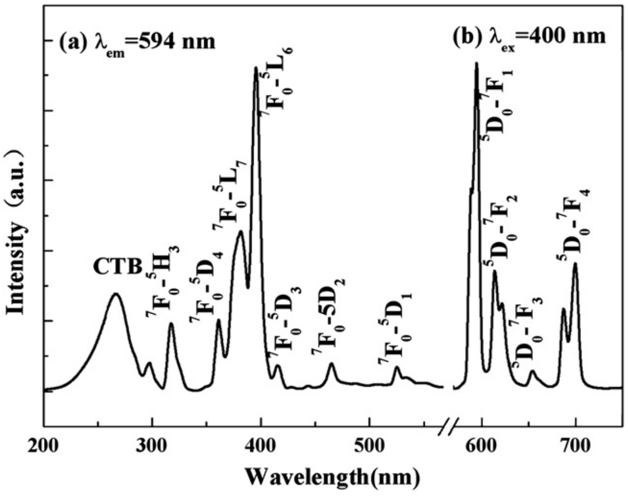

Fig. 4. Excitation and emission spectra of $Mg_{0.965}Al(PO_4)O$:0.035 Eu^{3+}.

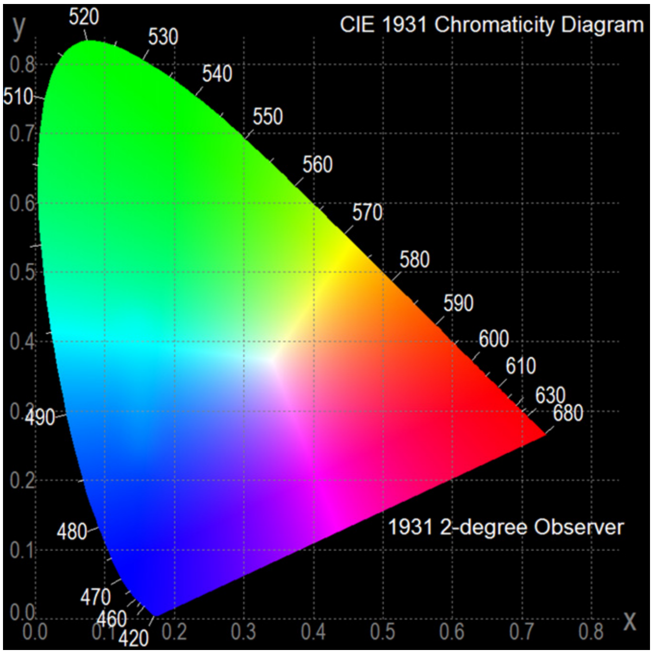

Fig. 5. Color coordinates of $Mg_{0.965}Al(PO_4)O$:0.035 Eu^{3+} in CIE chromaticity diagram. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

$^5D_0$–$^7F_2$ is the dominant transition. The result in Fig. 4 shows that the emission intensity of the $^5D_0$–$^7F_1$ transition is much stronger than the transition $^5D_0$–$^7F_2$, suggesting that the Eu^{3+} locate in an symmetric cation environment. Furthermore, considering the principles that ionic radii between doped and substituted ions should be as close as possible, we presume the doped Eu^{3+} may occupy the position of Mg^{2+} based on the crystal structure of $MgAl(PO_4)O$. On the other hand, the dominant emission of transition of $^5D_0$–$^7F_1$ resulting in Eu^{3+} activated compounds $MgAl(PO_4)O:Eu^{3+}$ showing strong reddish orange emission under 400 nm excitation. The color coordinates ($x=0.54$, $y=0.33$) of $MgAl(PO_4)O:Eu^{3+}$ in the Commission International ***de l'Eclairage* (*CIE*) *1931 chromaticit***y diagram is represented in Fig. 5, which indicate that $MgAl(PO_4)O:Eu^{3+}$ phosphor will be useful as orange–red luminescence materials.

The effect of doped-Eu^{3+} concentration on the emission intensity and the concentration quenching of $Mg_{1-x}Al(PO_4)O:xEu^{3+}$ are also investigated. The variations of PL intensity ($^5D_0\rightarrow{}^7F_2$ transition of Eu^{3+}) with different a Eu^{3+} content are shown in Fig. 6. The intensity of the emission transition was found to increase with an increase in the Eu^{3+} concentration up to 0.35 mol%, and then it decreases because of concentration quenching.

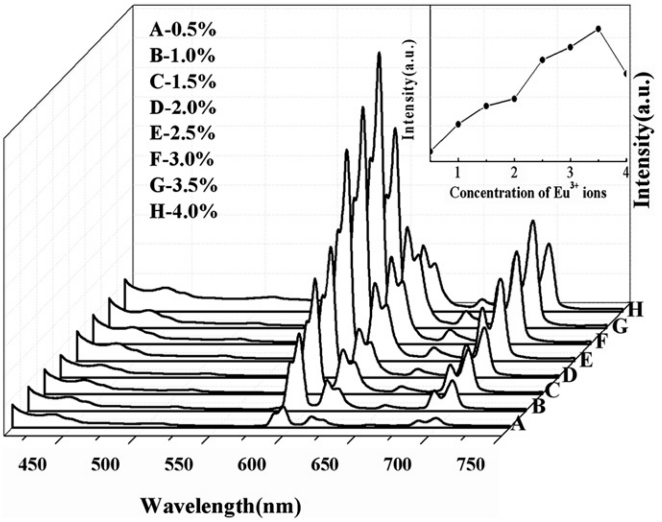

Fig. 6. Emission spectra of MgAl(PO$_4$)O:Eu^{3+} with a different Eu^{3+} concentration. (The inset plot gives the relation between the luminescent intensity and concentration of Eu^{3+} ions).

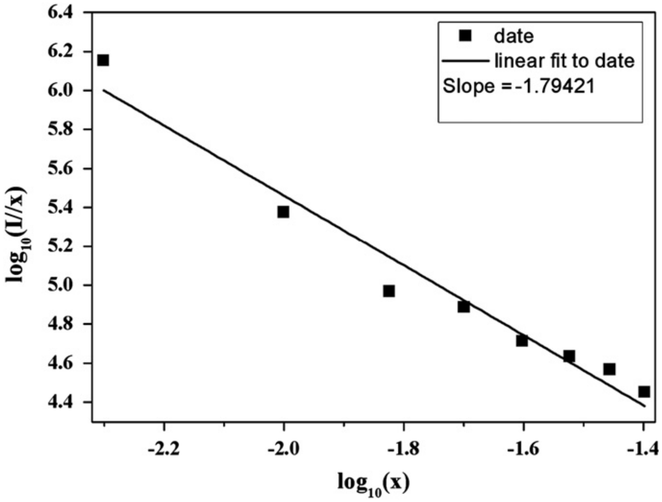

Fig.7. Relation between the log$_{10}$(I/x) and log$_{10}x$ of Eu^{3+} for Mg$_{1-x}$Al(PO$_4$)O:xEu^{3+}.

According to the report of Van Uitert, if the energy transfer takes place between the same sorts of activators, the intensity of multipolar interaction can be determined based on the change of the emission intensity from the emitting level which has the multipolar interaction [23]. The emission intensity (I) per activator ion follows the equation:

$$\frac{I}{x} = K[1+\beta(x)^{\theta/3}]^{-1} \tag{1}$$

where x is the concentration of the activator, K and β are the constants for a given excitation wavelength ($\lambda_{\mathrm{ex}}=394$ nm) and the crystal structure. The values of θ are 6, 8, and 10 mean dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interaction, respectively [23–25]. Eq. (1) can be approximately reduced to Eq. (2) for $\beta(x) \gg 1$[24]

$$\frac{I}{x} = K'\left[\beta(x)^{\theta/3}\right]^{-1} \tag{2}$$

where K' is a constant. Since the critical concentration of Eu^{3+} can be estimated as 3.5% from the inset of Fig. 6, the dependence of emission intensity on the doped-Eu^{3+} concentration based on Fig. 6 is shown in Fig. 7. Obviously, an approximately linear relation between log$_{10}$(I/x) and log$_{10}$(x) can be found, whose slope is about -1.882. The θ value can be calculated as 5.646 based on the linear fitting using Eq. (2), which is close to 6. This value indicates that the concentration quenching mechanism of Mg$_{1-x}$Al(PO$_4$)O:xEu^{3+} phosphors is dipole–dipole interaction. Although the intensity measurement of spectrum is an effective way to assume the concentration quenching mechanism of rare earth doped phosphor, the approach based on lifetime measurements may give a more accurate analysis due to less influence by experimental conditions [26], which will be considered in further investigation.

4. Conclusion

In the present work, a novel red-emitting phosphor Eu^{3+}-doped MgAl(PO$_4$)O has been synthesized by a conventional high temperature solid state method. The phosphors exhibit a red emission with the strongest emission peak at 594 nm, and the optimum concentration of luminescence is found to be 3.5% mol, which is quenched by the mechanism of dipole–dipole interaction. The results indicate that the MgAl(PO$_4$)O:Eu^{3+} is a potential phosphor for UV LED.

Acknowledgments

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