Al
3+
 Impacting on Eu
3+
 - Host Energy Transfer and Calculation of Eu
3+
 5D0 Quantum Efficiency

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Abstract—With 2 mol% Al
3+
 ions and 8 mol% Eu
3+
 ions co-doping, nano-size [K0.8Y0.63Eu3+0.08Al0.02][Mo0.2W0.8O4] phosphor was synthesized by the sol-gel method. Through XRD, DTA-TG, SEM and photoluminescent analysis, its morphology, crystal structure and luminescent property were discussed and it is found that one type of excellent phosphor can be obtained, and its luminescent efficiency and particles sizes can be improved to some extent by adjusting suitable technological conditions. According to the photoluminescent characteristics of the phosphor, its emission mechanism was mentioned. The partial J-O parameters and quantum efficiency of Eu
3+
 5D0 energy level were calculated under 395 nm excitation. The phosphor can combine with 390–410 nm InGaN chip in order to get different simple color light and white light. Under 20 mA forward-bias current, bright red light is observed by naked eyes so the phosphor will have excellent application outline from the LED illumination and display in the further.

Keywords—co-doping; energy transfer; J-O parameters; quantum efficiency; red LED

I. INTRODUCTION

To date, many efforts have been devoted to develop high-efficient red phosphors [1-3]. In particular, Eu
3+
 ions doped molybdates and tungstates in near-UV-based LEDs application have attracted many interests because of their doped molybdates and tungstates in near-UV-based LEDs from high photon flux and luminescence quenching in high-efficient red phosphors [1-3]. In particular, Eu
3+
[Mo
3+
, W
4+
O4] phosphor was synthesized by the sol-gel method. Through XRD, DTA-TG, SEM and photoluminescent analysis, its morphology, crystal structure and luminescent property were discussed and it is found that one type of excellent phosphor can be obtained, and its luminescent efficiency and particles sizes can be improved to some extent by adjusting suitable technological conditions. According to the photoluminescent characteristics of the phosphor, its emission mechanism was mentioned. The partial J-O parameters and quantum efficiency of Eu
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II. EXPERIMENTAL METHODS

Eu
3+
-Al
3+
 co-doped [K0.8Y0.63Eu3+0.08Al0.02][Mo0.2W0.8O4](KYEAMW)(total amount, 0.005 mol) was prepared by co-precipitation. A mixture of stoichiometric KNO3 (AR), Y(NO3)3 (AR), Eu(NO3)3 (99.99% purity, 8 mol%), and Al(NO3)3 (AR, 2mol%) was dissolved in 30 ml distilled water. Ammonium molybdate ((NH4)6Mo7O24·4H2O, AR) and ammonium tungstate ((NH4)2H7Mo7O24·4H2O, AR) were dissolved in 50 ml distilled water and the PH of solution was adjusted to 1.2-1.4 with diluted HNO3. The Eu
3+-Al
3+
 solution was slowly poured into W-Mo solution dropwise to form a clear and homogeneous solution. The solution was neutralized with precipitation agents (NH4)2CO3 and deposit the precursor at 78. The precursor was washed in distilled water several times and put into the drying cabinet for drying at 90 °C for 2 hours. Finally, the dried and ground it into powder, namely KYEAMW. All reagents were bought from Sinopharm Chemical Reagent Co., Ltd.

The structure of KYEAMW was recorded by X-ray powder diffraction (XRD) employing CuKα radiation at 40kV and 250mA. A step size of 0.02 degree (2theta) was used with a scan speed of 4 degrees/min. Thermo-gravimetric analysis (TG) and differential thermal analysis (DTA) were carried out simultaneously using a TG-DTA92 instrument (SETARAM, France). About 5 mg the precursor of KYEAMW were weighed in alumina crucible and first isothermally heated to 30°C for 2 min, and subsequently heated from 30 to 1050°C in a dynamic air atmosphere (air flow 5 L/h). The heating rate was 15°C / min. The furnace was calibrated using transition temperature of indium and aluminum. Calcined caolinites were used as reference materials. Excitation and emission spectra were measured by using a Hitachi F-4600 spectrometer equipped with a 150 W-xenon lamp under a working voltage of 500 V. The excitation and
emission slits were set at 2.5 nm and scanning speed was 1200nm/min. All the measurements were performed at room temperature.

III. RESULTS AND DISCUSSION

Fig. 1(a) indicates the XRD pattern of KYEAMW, of which the crystal structure is consistent with JCPDS card No. 29-0351, corresponding to the intrinsic diffraction patterns of CaMoO$_4$, a tetragonal crystal structure with space group of I4/a(88). Fig. 1(b) depicts the TG-DTA curves of the precursor of KYEAMW. The first weight loss stage is from room temperature to 700°C or so, corresponding to the endothermic peak at about 415 °C, which is associated with water loss and gel decomposed into oxides with network structure. The second weight loss stage is no weight loss from 700 to 1050 °C, corresponding to the endothermic peak at 820 °C or so, which is attributed to the crystalization and crystal particles growth of KYEAMW.

![Figure 1. XRD pattern of KYEAMW(a) and DTA curve(1) and TG curve(2) of the precursor of KYEAMW(b)](image)

In the present study, the relative PL intensity of Eu$^{3+}$ ion is more with 2 mol% Al$^{3+}$ ions and the host is composed of central Mo$^{6+}$/W$^{6+}$ ions binding with O$^{2-}$ ions. In the breathing model of the optical center, the ligand pulsates, away from the central ion, and a harmonic oscillator mode can describe the pulsations. The energy of the optical center, including the vibrational energy of the ligand, is depicted by lines in the configurational coordinate diagram (CCD).

Table 1 shows the average energies (cm$^{-1}$) and emission peaks corresponding to tungstate or molybdate is...
indicates that the Eu$^{3+}$ ion occupies non-centrosymmetric site in KYEAMW.

As far as the Eu$^{3+}$ 5D$_0$ $\rightarrow$ 7F$_j$ (J = 0-6) transition is concerned, 5D$_0$ $\rightarrow$ 7F$_{5,4,6}$ electric dipole transitions, 5D$_0$ $\rightarrow$ 7F$_3,5$ contain both electric dipole and magnetic dipole transition components. 5D$_0$ $\rightarrow$ F$_{3,4}$ transitions are forbidden for both electric dipole and magnetic dipole transitions and farther in the infrared region. So the emission of 5D$_0$ $\rightarrow$ F$_{5,6}$ transitions cannot be observed in the experiments.

In order to characterize transition rate between different energy levels of Eu$^{3+}$ ions, two transition intensity parameters $\Omega_j$ ($\lambda$ = 2, 4), called J-O parameters, are introduced into Judd-Ofelt theory. $\Omega_j$ can be influenced by environment around Eu$^{3+}$ ions. Especially, $\Omega_2$ has a close relationship to the environment around Eu$^{3+}$ ions. For K-Y-Mo-W host, $\Omega_2$ reflects structure symmetry, order property and covalent character of K-Y-Mo-W interaction. In a word, the host system which has larger $\Omega_2$ is in a more polarizable chemical environment and has stronger covalent character of K-Y-Mo-W interaction. Thus, transition intensity parameters can help us to know the lattice-sites occupied by Eu$^{3+}$ ions in K-Y-Mo-W host and the micro-environment around Eu$^{3+}$ ions.

Quantum efficiency of Eu$^{3+}$ 5D$_0$ energy level can also be calculated by experimental data. The fluorescence lifetime $\tau$ of 5D$_0$ radiative transition rate $A_R$ and non-radiative transition rate $A_N$ can be expressed as follows:

$$\frac{1}{\tau} = A_R + A_N \quad (1)$$

where $A_R$ is the sum of each 5D$_0$ $\rightarrow$ 7F$_j$ ($J$ = 1, 2, 4) transition rate, viz. $\sum_{J=1,2,4} A_{0-J}$. $A_{0-J}$ is the energy barycenter of the 0-J transition. Here $A_{0-J}$ is the experimental coefficients of spontaneous emissions, $A_{0-J}$ is the Einstein’s coefficient of spontaneous emission between the 5D$_0$ and 7F$_j$ energy levels, which can be determined as approximately 50 s$^{-1}$ and as a reference to calculate the value of other $A_{0,J}$[16-17]. So the quantum efficiency of Eu$^{3+}$ 5D$_0$ energy level can be expressed by

$$\eta = \frac{A_R}{A_R + A_{NR}} = \tau \sum_{J=1,2,3,4} A_{0-j} \quad (2)$$

Fluorescence decay curves (measuring luminescence of 5D$_0$ $\rightarrow$ 7F$_2$) of 5D$_0$ energy level are measured under 395 nm excitation. The fluorescence decay curves are fitted by exponential decay to obtain the values of $\tau$. Then the value of $\eta$ would be obtained by Eq. (2). TABLE II depicts the average energies (cm$^{-1}$) and emission peaks situation/area of Eu$^{3+}$ 5D$_0$ $\rightarrow$ 7F$_{J}(J=0-4)$ of KYEAMW and TABLE II shows the values of $\tau$, $A_R$, $A_{R+}$, $A_{NR}$ $\eta$ and so on of KYEAMW. According to Judd-Ofelt theory, 5D$_0$ $\rightarrow$ 7F$_1$ magnetic dipole transition rates can be represented by $A_{0,1}$ is the Einstein’s coefficient of spontaneous emission from 5D$_0$ $\rightarrow$ 7F$_1$, which can be determined as approximately 50 s$^{-1}$ and as a reference to calculate the value of other $A_{0,J}$[15-16].

$$A_{0-0} = A_{0-1}(S_{0-0} / S_{0-1})(\nu_{0-0} / \nu_{0-1}) = 4.1 \text{ s}^{-1},$$
$$A_{0-2} = A_{0-1}(S_{0-2} / S_{0-1})(\nu_{0-2} / \nu_{0-1}) = 204.7 \text{ s}^{-1},$$
$$A_{0-4} = A_{0-1}(S_{0-4} / S_{0-1})(\nu_{0-4} / \nu_{0-1}) = 21.7 \text{ s}^{-1},$$
$$A_{0-5} = A_{0-0} + A_{0-1} + A_{0-2} = 280.5 \text{ s}^{-1},$$
$$A_{0-6} = A_{0-0}/(1/\tau - 0.558 - 1792.1) = 15.7\%.$$
\[ \langle \mu \Omega \| U^J \| \nu' J' \rangle^2 \] is squared reduced matrix element of transition from \( \nu' J' \) to \( \nu J \).

Thus the ratio between electric dipole transition rate and magnetic dipole transition rate can be expressed as follows.

\[
\frac{\Omega_{0J}}{\Omega_{md}} = \frac{e^2 k^3}{S_{md} k_{md}} \left( \frac{n^2 + 2}{9n^2} \right) \Omega_j \langle \mu \Omega \| U^J \| \nu' J' \rangle^2
\]

(4)

Transition rate of each energy level is in direct proportion to integral intensity of emission spectrum in Table I. where \( k_{md} \) is wavenumber of \( ^3D_0 \rightarrow ^3F_1 \) transition, \( k_j \) is wavenumber of \( ^3D_0 \rightarrow ^3F_j \), \( n \) refractive index of host \( 1.6 [17] \), \( h \) Planck constant, \( J' \) equals zero for the \( ^3D_0 \rightarrow ^3F_1 \) and \( S_{md} \) is line strength of \( ^3D_0 \rightarrow ^3F_1 \) transition. Because linear strength of magnetic dipole transition nearly can’t be influenced by outer environment, the value of \( S_{md} \) for a certain transition has no relation with the hosts and it is a constant. \( S_{md} \) is calculated to be \( 7.83\times10^{-22} \) esu(cm) \(^2\) through the data in literature [18]. \( \langle \mu \Omega \| U^J \| \nu' J' \rangle^2 \) values are the square reduced matrix elements whose values are 0.0032 and 0.0023 for \( J=2 \) and 4 [16]. All parameters in this section used Gauss system of units. Then, according to Eq. (4), \( \Omega_j \) can be calculated by utilizing emission spectrum. Table 3 shows the values of \( \Omega_j \) and \( \Omega_{0J} \) for \( \Omega_j = 5.46\times10^{-20} \) (cm\(^2\)) and \( \Omega_{0J} = 1.45\times10^{-20} \) (cm\(^2\)). Moreover, the higher emission quantum efficiency is obtained from the KYEMW phosphors (\( \eta = 15.7 \%) \) than in KYEMW phosphors (\( \eta = 13.92 \% \)), which is due to appreciably decrease in non-radiative decay rates from the \( ^3D_0 \) level.

IV. CONCLUSIONS

With 2 mol % Al\(^{3+} \) ions and 8 mol% Eu\(^{3+} \) ions co-doping \([K_{0.8}Y_{0.65}Eu^{3+}_{0.05}Al_{0.02}][MoO_3W_{0.8}O_4]\) nano-powder with good luminescent properties can be synthesized by co-precipitation method and its possible energy transfer mechanism are mentioned. According to the characteristics of reduced matrix for \( ^3D_0 \rightarrow ^3F_2, 4 \) transitions, J-O transition parameters \( \Omega_j \) and \( \Omega_{0J} \) can be calculated, \( \Omega_j = 5.46\times10^{-20} \) (cm\(^2\)) and \( \Omega_{0J} = 1.45\times10^{-20} \) (cm\(^2\)), and energy transfer efficiency between Eu\(^{3+} \) ions and WO\(_3\)/MoO\(_4\) groups is improved, \( \eta = 15.7 \% \) (compared to \([K_{0.8}Y_{0.65}Eu^{3+}_{0.05}][MoO_3W_{0.8}O_4]\), \( \eta = 13.92 \%) \).

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