Novel red-emitting $\text{Lu}_3\text{Te}_2\text{Li}_3\text{O}_{12}$: Eu^{3+} phosphor with high color purity for n-UV WLEDs

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Abstract. In this work, a series of red emitting $\text{Lu}_3\text{Te}_2\text{Li}_3\text{O}_{12}$: Eu^{3+} phosphors were synthesized for the first time by high temperature solid state reaction. The structure was characterized by X-ray diffraction. The excitation spectra, emission spectra and CIE chromaticity coordinate were studied. The phosphors show strong red emission at 611 nm due to the $^5\text{D}_0$ - $^7\text{F}_2$ transition of Eu^{3+} ions. The optimal doping concentration of Eu^{3+} in LTL host is $x = 0.5$ due to the concentration quenching mechanism of dipole-dipole interaction. The CIE chromaticity coordinates of the LTL: 0.5Eu^{3+} phosphor is (0.644,0.355), and the purity of the color is up to 93.61%. The phosphor can be considered as a potential red-emitting candidate for near UV WLEDs.

1 Introduction

With the continuous enhancement of people's awareness, the exploration of new technologies to meet these needs has become a research hotspot in the field of lighting. [1-4] In the past decades, white light emitting diodes (WLEDs) have been considered as the next generation of solid-state light sources due to their advantages of energy saving, environmental protection and long life. At present, the commercial way to produce white light is to combine blue light chip (InGaN) with yellow phosphor $\text{Y}_3\text{Al}_5\text{O}_{12}$: Ce^{3+} (YAG: Ce^{3+}). Although owning many advantages, this method is limited due to the lack of red emission and low color rendering index ($\text{CRI} < 80$), which goes against its application in the environment with the requirements for high color rendering, such as indoor, hospital and museum. Recently, the combination of near ultraviolet (n-UV) LED chips and red-, green- and blue-emitting phosphors to obtain warm white light become an effective way to solve the above problem. However, the existing commercial red phosphors, such as nitrides or sulfides, have either harsh synthesis conditions or poor chemical stability. Therefore, it is of great significance to develop novel oxide red phosphors with good chemical stability, high efficiency and convenient synthesis.

The garnet-type compound with the formula of $\text{A}_3\text{B}_2\text{C}_3\text{O}_{12}$ possess the characteristics of stable lattice and high thermal conductivity, which is considered as a potential host for optical materials.[5-7] Although many famous phosphors with garnet structure have been widely studied and applied, such as yellow phosphors $\text{Y}_3\text{Al}_5\text{O}_{12}$: Ce^{3+} , green phosphors $\text{Lu}_3\text{Al}_5\text{O}_{12}$: Ce^{3+} and $\text{Ca}_3\text{Sc}_2\text{Si}_3\text{O}_{12}$: Ce^{3+} , etc., the red emitting garnet-type phosphors have been rarely reported.

In this work, a series of $\text{Lu}_3\text{Te}_2\text{Li}_3\text{O}_{12}$: $x\text{Eu}^{3+}$ (LTL: Eu^{3+}) phosphors were successfully prepared using high temperature solid-state reaction in air atmosphere. The crystal structure, photoluminescence (PL) properties, CIE chromaticity coordinates and color purity of the samples have been systematically studied. The results show that, $\text{Lu}_3\text{Te}_2\text{Li}_3\text{O}_{12}$: $x\text{Eu}^{3+}$ phosphors with high color purity have broad application prospects for UV-pumped WLEDs.

2 Experimental Section

A series of Eu^{3+} ions activated $\text{Lu}_3\text{Te}_2\text{Li}_3\text{O}_{12}$: $x\text{Eu}^{3+}$ compounds have been prepared by a traditional high temperature solid-state reaction in air. In a representative preparation process, the appropriate amount of raw materials was weighed and mixed together according to stoichiometric mole ratio as following: Lu_2O_3 (99.99%), TeO_2 (A.R.), Li_2CO_3 (A.R.) and Eu_2O_3 (99.99%). After full grounding in an agate mortar, the final mixed powder was transferred to into the alumina crucible and preheated at 500 °C for 1 hour. And then the mixture was reground and sintered at 900 °C for 5 hours. The obtained product was naturally cooled down to room temperature, grounded into powder for further characterization. The X-ray diffraction (XRD) patterns of the sample were examined by Rigaku/Ultima IV X-ray diffractometer within 2θ range from 10° to 80° . The photoluminescence spectrum and photoluminescence excitation spectrum were measured by a Hitachi F-7000 fluorescence spectrophotometer equipped with a 150W Xe lamp.

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3 Results and Discussions

The XRD patterns of LTL: $x\text{Eu}^{3+}$ ($x=0.1, 0.3, 0.4, 0.6, 0.8$ and 1.0) were shown in Fig.1(a). All of the patterns are consistent with $\text{Lu}_3\text{Te}_2\text{Li}_3\text{O}_{12}$ (PDF#26-1170) in the International Centre for Diffraction Data (ICDD) database, which exhibited as garnet-type structure and correspond to the $\text{Ia}\bar{3}\text{d}$ space group of the cubic system. No other diffraction peaks of raw materials or impurities are observed in the patterns. The enlarged diffraction peaks at the range of 35.6° – 36.4° were presented in Fig. 1(b). In addition, with dropping Eu^{3+} in host, it is obvious that the main diffraction peak (crystal face (4 2 0)) of the sample moves to a lower angle, indicating that lattice expands due to the doping of rare earth ions in LTL host and the offset increases with the doping amount and the size of rare earth ions. According to the above-mentioned phenomenon, it demonstrates that Eu^{3+} ions are successfully doped into the matrix, the pure LTL phase can be synthesized under this sintering condition.

Fig. 1. (a) XRD patterns of the LTL: $x\text{Eu}^{3+}$ ($x=0.1, 0.3, 0.4, 0.6, 0.8$ and 1.0) phosphors and the standard data of $\text{Lu}_3\text{Te}_2\text{Li}_3\text{O}_{12}$ (PDF card No.26-1170); (b) the enlarged XRD patterns of samples from 35.6° to 36.4° ; (c) Crystal structure and local coordination of the $\text{Lu}_{1-x}\text{Te}_2\text{Li}_3\text{O}_{12}: x\text{Eu}^{3+}$ samples.

Fig. 1(c) shows the model of crystal structure and local coordination of the $\text{Li}_3\text{Te}_2\text{Lu}_3\text{O}_{12}: \text{Eu}^{3+}$, Lutecium ions were located in 24c Wyckoff sites to form $[\text{LuO}_8]$ distorted dodecahedron, Te^{6+} and Li^+ ions are distributed in 16a and 24d Wyckoff sites respectively to form $[\text{TeO}_6]$ octahedron and $[\text{LiO}_4]$ tetrahedron. The ionic radii for Lu^{3+} , Te^{6+} and Li^+ are 97.9 pm, 56 pm and 59 pm, respectively. Owing to the similar cationic radius and valence, the RE ion dopant Eu^{3+} (107pm) were expected to replace the Lu^{3+} sites more than Te^{6+} and Li^+ in the host. The fitted cell parameters of samples are listed in Table 1. With the increase of Eu^{3+} content, the values of the lattice parameters(a) and cell volume (V) increased obviously. This is consistent with the low angle shift of the main diffraction peak in Fig.1(b).

Table 1. The fitted values of cell parameters of $\text{Lu}_3\text{Te}_2\text{Li}_3\text{O}_{12}: x\text{Eu}^{3+}$ ($x = 0.1, 0.3, 0.4, 0.6, 0.8$ and 1.0).

x	a(Å)	V(Å ³)	x	a(Å)	V(Å ³)
0.1	12.17	1803.226	0.6	12.23	1829.274
0.3	12.19	1813.615	0.8	12.25	1839.764
0.4	12.21	1818.825	1.0	12.28	1850.294

Fig. 2(a) and (b) display the typical excitation spectrum and emission spectrum of LTL: 0.1Eu^{3+} phosphors excited at 395 nm and monitored at 611 nm. Monitored at the optimum emission wavelength of 611nm, a broad band ranging from 200 nm to 290 nm and some narrow emission lines in the ultraviolet and visible spectral areas can be observed in Fig. 2(a). The band peaking at 256 nm are assigned to the charge-transfer state transition of $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$ ligand-to-metal. A sequence of sharp excitation bands located at 320nm, 362nm, 383nm, 395nm, 417nm, 464nm, 526nm and 536nm in the wavelength region from 300 nm to 550 nm belongs to the spin-forbidden $^7\text{F}_0 \rightarrow ^5\text{H}_6$, $^5\text{D}_4$, $^5\text{L}_{7,8}$, $^5\text{G}_J$, $^5\text{L}_6$, $^5\text{D}_{3,2,1,0}$ and $^7\text{F}_1 \rightarrow ^5\text{D}_1$ transition of Eu^{3+} ions [8]. It is worth noting that the excitation peak at 395 nm exhibits the secondary intensity, demonstrating that LTL: Eu^{3+} phosphor can be used for WLED devices excited by n-UV. Upon the excitation of 395 nm, the PL spectrum shows a series of emission peaks centering at 570, 594, 611, 656 and 709 nm, which are assigned to the spin-forbidden $4f \rightarrow 4f$ transition of Eu^{3+} , namely $^5\text{D}_0 \rightarrow ^7\text{F}_{0,1,2,3,4}$ energy transition. Obviously, the emission intensity peaking at 613 nm attributed to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition is the strongest. In general, R is used to evaluate the positional symmetry of Eu^{3+} ions, which can be calculated by Formula $R = I(^5\text{D}_0 \rightarrow ^7\text{F}_2) / I(^5\text{D}_0 \rightarrow ^7\text{F}_1)$ is based on the measured PL emission spectrum [9]. The R-value was about 4.409 in LTL: 0.1Eu^{3+} sample, which indicated that Eu^{3+} ion replaced the asymmetric site of LTL host.

Fig. 2. (a) Excitation spectrum ($\lambda_{em}=611\text{ nm}$) and (b) emission spectrum ($\lambda_{ex}=395\text{ nm}$) of LTL: $x\text{Eu}^{3+}$ phosphors.

The relationship between PL intensity and Eu^{3+} concentration in LTL: $x\text{Eu}^{3+}$ ($x=0, 0.1, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$ and 1.0) is depicted in Figure 3(a) and its inset. It can be observed that the profile of all samples doped with different ionic contents of Eu^{3+} are similar. As shown in the inset, under 395 nm excitation, with the increase of Eu^{3+} concentration, the emission intensity increases continuously, reaches the maximum value at $x = 0.5$, and then begins to decline. The reason for the decrease of emission intensity is attributed to the effect of concentration quenching, which is caused by the non-radiative energy transfer within the nearest Eu^{3+} ions. According to the theory of resonance energy transfer reported by Reisfeld's group, energy transfer among activator ions in the following ways: the exchange interaction or electric multipolar interaction [10]. Whether or not the exchange interaction mechanism is responsible for energy transfer relies mainly on the critical distance (R_c) in host. Generally speaking, exchange interaction may occur with R_c value less than 5 Å. On the contrary, if the value of R_c is larger than 5 Å, the electric multipolar interaction may be dominant. Therefore, as an important parameter, R_c can be estimated via the Blasse's equation as follow [11]:

$$R_c = 2(3V/4\pi x_c N)^{1/3} \quad (1)$$

Here $N = 24$, which represents the maximum number of sites occupied by rare-earth ions in the unit cell and $V \approx 1824.79 \text{ Å}^3$, which refers to the volume of the crystal cell, and x_c refers to the concentration of Eu^{3+} ions at which the energy transfer efficiency is approximately 0.5. Taking the above parameters into formula (1), it can be calculated that R_c is 6.62 Å. The value of critical distance larger than 5 Å state clearly that the main reason of energy transfer among activated Eu^{3+} ions in this system depended on the electric multipole interaction.

Fig. 3. (a) Dependence of emission intensity on doping concentration of Eu^{3+} and (b) the $\lg(I/x)$ - $\lg x$ plot with linear fitting for LTL: $x\text{Eu}^{3+}$ phosphors.

To determine the mechanism of concentration quenching between activator ions, Dexter proposed that the relationship between the emission intensity of the sample and the doping content of the activator is given by the equation as follow

$$I/x = k[1 + \beta(x)^{\theta/3}]^{-1} \quad (2)$$

here, x stands for the activator concentration of Eu^{3+} ion after the concentration quenching, the I is integrated luminescence intensity, k and β are constants for each type of interaction for a given host lattice under the same excitation condition. θ is a constant of multipolar interaction and equals 6, 8, or 10 corresponding to the nearest-neighbor ions corresponding to dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interactions, respectively.

As depicted in Fig. 3(b), the relation between $\log(I/x)$ on $\log(x)$ was found to be relatively linear, with the slope fitted to be -1.27. Accordingly, the value of y was calculated to be 3.81, and hence found to be closest to the above value of 6, indicating that the concentration quenching should be caused by dipole-dipole interaction for Eu^{3+} ion in the LTL host.

Fig. 4 presented the CIE chromaticity coordinates of LTL: $x\text{Eu}^{3+}$, commercial $\text{Y}_2\text{O}_3\text{S: Eu}^{3+}$ phosphor and standard red light. It can be seen that, as the increasing ratio of Eu^{3+} , the CIE coordinates are gradually migrated from (0.640, 0.360) to (0.645, 0.354), which is better than that of the commercial $\text{Y}_2\text{O}_3\text{S: Eu}^{3+}$ red phosphor (0.622, 0.351) and very close to the National Television Standard Committee standard value (0.670, 0.330). In addition, the color purity is an important index to measure the properties of phosphors, which can be

calculated by the expression described by Fred Schubert [12]:

$$\text{Color purity} = [(x_s - x_i)^2 + (y_s - y_i)^2]^{1/2} / [(x_d - x_i)^2 + (y_d - y_i)^2]^{1/2} \quad (3)$$

where (x_s, y_s) represents the CIE coordinate of the samples with various Eu^{3+} concentrations, (x_i, y_i) stands for the color coordinate of the white illumination and the (x_d, y_d) is the chromaticity coordinates of the dominant wavelength.

Table 2. The CIE chromaticity coordinates and color purity of LTL: $x\text{Eu}^{3+}$ phosphors.

Eu^{3+} concentrations(mol)	CIE chromaticity coordinates		Color purity (%)
	x	y	
0.1	0.640	0.360	92.68
0.3	0.643	0.356	93.37
0.5	0.644	0.355	93.61
0.7	0.645	0.355	93.89
1.0	0.645	0.354	93.86

As shown in Table 2, the result of calculation reveals that the LTL: $x\text{Eu}^{3+}$ phosphors possess high color purity and excellent chromaticity coordinate characteristics. The results show that the sample has high color purity and excellent chromaticity coordinate characteristics. As shown in the illustration in Fig. 10, the strong red emission of LTL: 0.5Eu^{3+} sample is observed by the digital camera under 365 nm UV irradiation.

Fig. 4. Typical CIE chromaticity coordinates of LTL: $x\text{Eu}^{3+}$ phosphors, $\text{Y}_2\text{O}_2\text{S: Eu}^{3+}$ and standard red light and the inset shows the photograph of LTL: 0.5Eu^{3+} .

4 Conclusions

A new type of red phosphor $\text{Lu}_3\text{Te}_2\text{Li}_3\text{O}_{12}: x\text{Eu}^{3+}$ was prepared by high temperature solid state method. The results show that the phosphor can be effectively excited by near ultraviolet light and emit strong red emission. The optimal dopant concentration of Eu^{3+} is about 0.5. The critical distance of Eu^{3+} is 6.62 Å. The reason of

concentration quenching mechanism in LTL was confirmed to be dipole-dipole interaction among the nearest ions. Eu^{3+} -doped LTL phosphors with outstanding CIE chromaticity coordinates and color purity are potential red phosphors for WLED.

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