Luminescence of Tb$^{3+}$/Eu$^{3+}$ codoped LiYF$_4$ single crystals under UV excitation for white-light LEDs

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The absorption spectra, excitation spectra, and emission spectra of Tb$^{3+}$/Eu$^{3+}$ ions in LiYF$_4$ single crystals synthesized by an improved Bridgman method are measured. The emission spectra of several bands, mainly located at blue $\sim$487 nm (Tb:5D$_{4} \rightarrow$ 7F$_{6}$), yellowish green $\sim$542 nm (Tb:5D$_{4} \rightarrow$ 7F$_{5}$), and red $\sim$611 nm (Eu:5D$_{0} \rightarrow$ 7F$_{2}$) wavelengths, are observed under excitation by UV light. An ideal white light emission as a result of simultaneous combination of these emissions can be obtained from 1.11 mol% Tb$^{3+}$ and 0.9 mol% Eu$^{3+}$ co-doped LiYF$_4$ single crystals with chromaticity coordinates of $x = 0.3242$, $y = 0.3389$, color temperature $T_c = 5878$ K, color rendering index $R_e = 77$, and color quality scale $Q_a = 75$ under excitation of 384 nm light. The chromaticity coordinate, color rendering index, and color quality scale can be modified by the change of the concentration of rare-earth dopants and the excitation wavelength.

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Recently, a significantly increasing interest has been drawn from rare-earth (RE) ion doped single-host full-color emitting solid state materials for achieving white light emission because they show superior properties such as high heat resistance, high luminous efficiency, low light scattering, and low power consumption which could overcome the weaknesses of using the common two commonly used methods to obtain white LEDs. As is well-known, under UV light excitation, Tb$^{3+}$ ions have transitions in the blue light region $\sim$487 nm ($^{5}D_{4} \rightarrow ^{7}F_{6}$) and yellowish green-light region $\sim$542 nm ($^{5}D_{4} \rightarrow ^{7}F_{5}$), while Eu$^{3+}$ ions can emit red light $\sim$611 nm ($^{5}D_{0} \rightarrow ^{7}F_{2}$). These full-color emissions including blue-, green-, and red-emitting light could potentially enable a near-ideal white light. Tb$^{3+}$/Eu$^{3+}$ ions co-doped glasses have been fabricated and white emitting light was obtained.

Besides the dopants of REs, the host material also plays a significant role in LED applications. Previous LED materials mainly focused on glasses[8,9], glass ceramics[10,11], and transparent ceramics[8]. Single crystals can be considered to be very favorable as the host materials for optical devices because they have high luminous efficiency, high mechanical strength, and excellent chemical durability. Recently, we prepared LiYF$_4$ single crystals co-doped with Tb$^{3+}$ and Dy$^{3+}$ for a white light emission. The single crystals have advantages of excellent thermal and mechanical properties, better transmittance, superior radiation resistance, as well as higher luminous efficiency. However, there are only a few reports about Tb$^{3+}$/Eu$^{3+}$ co-doped single crystals for white LED applications.

In this Letter, a LiYF$_4$ single crystal co-doped with Tb$^{3+}$/Eu$^{3+}$ was obtained by the modified Bridgman method, and the luminescence properties of the crystal were characterized, aimed at using it as a new potential host material for white LED applications.

LiYF$_4$ single crystals doped with Tb$^{3+}$ and co-doped with Tb$^{3+}$/Eu$^{3+}$ were successfully synthesized by a vertical Bridgman method. High-purity LiF, YF$_3$, TbF$_3$, and EuF$_3$ as feed materials without any preprocessing were prepared for crystals growth. The Li-rich composition could be beneficial for the growth of these transparent crystals. The molar composition of the single crystals was determined by the formulas Li$_{0.991}$Tb$_{0.009}$F$_4$ and Li$_{0-x-y}$Tb$_x$Eu$_y$F$_4$ ($x = 0.009, 0.010, 0.011, 0.011$, and $0.011; y = 0.008, 0.008, 0.008, 0.010, and 0.012$, respectively). Then the as-prepared mixture of raw materials was ground $\sim$1 h in a mortar. The moisture and the some oxygen impurities in the fluoride powders were removed completely using the high-temperature hydrofluorination method by which the powders were sintered with anhydrous HF at 800$^\circ$C for 8 h. The as-produced polycrystalline bars were fully ground in a mortar again and sealed in Pt crucibles sized $\Phi 10$ mm $\times$ 100 mm.
A detailed procedure for LiYF₄ single crystals was described elsewhere [1]. The as-grown crystals were cut into several pieces and then well-polished to ~2.0 mm thickness. The samples are very transparent and one of them (TE0) is shown in the inset of Fig. 1. The concentrations of the active ions in the samples were measured by inductively coupled plasma–atomic emission spectroscopy (ICP–AES, PerkinElmer Inc., Optima 3000) and the designated symbols for these samples and doping concentrations of rare earths are listed in Table 1.

An XD-98X diffractometer (XD-3) was used to identify the phase composition of the single crystal. The absorption spectra ranging from 300 to 600 nm were recorded with a Cary 5000 UV/visible/near-IR (NIR) spectrophotometer (Agilent). The luminescence properties of the crystals were characterized by the excitation and emission spectra measured on an F-4500 spectrophotometer (Hitachi High-Technologies). All measurements were executed at room temperature (RT).

Figure 1 displays the powder x-ray diffraction (XRD) pattern of the sample TE0 and the standard pattern of the LiYF₄ crystal (Joint Committee on Powder Diffraction (JCPD) No. 77-0816) [2]. The corresponding lattice plane indexes are also labeled in Fig. 1. The diffraction peaks of LiYF₄ single crystals co-doped with Tb³⁺/Eu³⁺ correspond well to those of standard LiYF₄ and have no visible shift compared with standard card JCPD No. 77-0816, indicating that the obtained doped crystal has a pure phase. The other samples also showed similar XRD patterns. It proves that small amount of dopants substituting the positions of Y³⁺ ions do not cause any meaningful change of the crystal structure. It also could be obtained that the sample TE0 has the scheelite (CaWO₄) structure and its lattice constants can be calculated as follows

\[ 2 - 2 \cos 2\theta = \lambda^2((h/a)^2 + (k/b)^2 + (l/c)^2), \]  

where \(2\theta\) is the diffraction angle in corresponding lattice plane indexes \((h, k, l)\), which have been marked in Fig. 1. \(\lambda\) is the Cu Kα radiation wavelength (\(\lambda = 0.15406\) nm), and a, b, and c are the lattice constants.

The results are as follows: a = b = 0.5173 nm, and c = 1.0764 nm, which is very close to the standard constants (a = b = 0.5171 nm, and c = 1.07484 nm) shown in Fig. 1.

Figure 2 displays the absorption spectra of Samples T0, TE0, and un-doped LiYF₄ crystals which are marked a, b, and c, respectively, ranging from 300 to 600 nm. Obviously, an un-doped LiYF₄ single crystal has no visible absorption peaks. It can be seen that at the Tb³⁺ singly doped T0 sample, the main absorption peaks are at ~352, ~358, ~369, ~377, and ~486 nm, which correspond to Tb³⁺ transitions from the 7F₅ ground state to the 5G5, 5L₉, 5G₆, 5D₃, and 5D₄ excited states. With respect to the Tb³⁺/Eu³⁺ co-doped TE0 sample, obviously additional peaks at ~319 and ~394 nm, which are ascribed to the Eu³⁺ ion transitions from the 5F₅ to the 5H₄ and 5L₆ excited states, appeared. All the corresponding transitions have been clearly marked in Fig. 2. The absorption spectrum of Sample TE0 shows that the crystal co-doped with Tb³⁺/Eu³⁺ ions can be excited simultaneously efficiently by UV light.

In order to investigate the luminescence properties of a Tb³⁺/Eu³⁺ co-doped LiYF₄ single crystal, the emission spectra of Samples T0 and TE0 under 374 nm excitation were measured and are displayed in Fig. 3. As shown in Fig. 3, the crystal TE0 can emit blue light around 413 and 436 nm, corresponding to 5D₃ → 7F₅ (J = 5, 4) transitions.

### Table 1. Concentrations of Tb³⁺ and Eu³⁺ Ions in LiYF₄ Single Crystals

<table>
<thead>
<tr>
<th>Symbols</th>
<th>T0</th>
<th>TE0</th>
<th>TE1</th>
<th>TE2</th>
<th>TE3</th>
<th>TE4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tb</td>
<td>0.85</td>
<td>0.84</td>
<td>0.95</td>
<td>1.10</td>
<td>1.11</td>
<td>1.11</td>
</tr>
<tr>
<td>Eu</td>
<td>0</td>
<td>0.60</td>
<td>0.60</td>
<td>0.61</td>
<td>0.75</td>
<td>0.90</td>
</tr>
</tbody>
</table>

*In units of mol%.*
of Tb$^{3+}$: a green–blue light near 487 nm, due to the electronic transition of Tb$^{3+}$ ($5D_4 \rightarrow 7F_6$); a green light near 542 nm (Tb$^{3+}$: $5D_4 \rightarrow 7F_5$); an orange light near 587 nm, which originates from the co-contribution of Tb$^{3+}$ and Eu$^{3+}$ due to the overlapped emissions corresponding to the $5D_4 \rightarrow 7F_4$ transition of Tb$^{3+}$ ions and the $5D_0 \rightarrow 7F_1$ transition of Eu$^{3+}$ ions; and a red light near 611 and 618 nm, ascribed to the transitions of Eu$^{3+}$ ($5D_0 \rightarrow 7F_2$) and Tb$^{3+}$ ($5D_4 \rightarrow 7F_3$) ions, respectively. All the transitions are labeled clearly in Fig. 3. The simultaneous emissions of blue, green, and red light enable white light to be possible from Tb$^{3+}$/Eu$^{3+}$ co-doped LiYF$_4$ crystals pumped by UV light.

Figure 4 presents the excitation spectra of Sample TE0 monitored at 487, 542, and 611 nm wavelengths ranging from 300 to 400 nm for obtaining an optimal excitation wavelength. The monitored spectra are named d, e, and f in Fig. 4, correspondingly. It can be obviously found that the intensity of the excitation peaks for Curve e is slightly stronger than that for Curve d. It indicates that the intensity of the emission peak at 542 nm is slightly stronger than that at 487 nm when excited by corresponding excitation wavelengths. The excitation spectrum for Curve f shows similar characteristic bands of Eu$^{3+}$ ions centering at 306, 318, 360, 380, and 394 nm, and its corresponding electronic transitions from the ground state $7F_0$ to excited states $3P_0$, $5H_4$, $5D_4$, $5G_2$, and $5L_6$, respectively. Four excitation bands peaking at 302 ($7F_6 \rightarrow 5H_6$), 318 ($7F_6 \rightarrow 5H_7$, $5D_0$), 353 ($7F_6 \rightarrow 5G_5$, $5D_2$, $5G_4$, $5L_0$, $5G_3$, $5L_8$), and 374 nm ($7F_6 \rightarrow 5D_3$, $5L_{10}$) are included in the excitation spectrum of Tb$^{3+}$ for Curve d. Moreover, Curve e shows the similar excitation spectrum to Curve d. As shown in Fig. 4, the excitation wavelengths at 353, 362, 374, and 384 nm were chosen to obtain a better white light emission. Figure 5 shows the emission spectra of Sample TE0 ranging from 400 to 760 nm under the excitation wavelengths 353, 362, 374, and 384 nm, respectively. When excited by those wavelengths, the emission spectra show similar bands while the luminous intensities are changed with the excitation wavelengths. The related electronic transitions have been discussed previously in the context of Fig. 3.

The different concentrations of dopants in LiYF$_4$ single crystals were prepared for obtaining an optimum white light emission. Figure 6 displays the fluorescence spectra of the samples TE$i$ ($i = 0$–4) under 384 nm excitation wavelength. It can be clearly found that the emission...
peaks of the samples are similar with a slight difference in luminous intensities. One can state that emission intensities change with concentrations of Tb$^{3+}$ and Eu$^{3+}$ ions in LiYF$_4$ single crystals. This luminous phenomenon implies a complicated process of energy transition between the Tb$^{3+}$ and Eu$^{3+}$ ions in the host material.

It is necessary to mark chromaticity coordinates of the samples on a standard chromaticity diagram for reflecting their luminescence color which is shown in Fig. 7. The chromaticity coordinates for the emissions of the samples TE$i$ ($i = 0–4$) under 384 nm excitation wavelengths can be calculated using the following:

$$
x = \frac{X}{X + Y + Z}, \quad y = \frac{Y}{X + Y + Z}, \quad z = \frac{Z}{X + Y + Z},$$  

where $X$, $Y$, and $Z$ are three tristimulus values. Those three values are given by the following:

$$X = \int_\lambda P(\lambda)\bar{\varepsilon}(\lambda) d\lambda, \quad Y = \int_\lambda P(\lambda)\bar{\gamma}(\lambda) d\lambda, \quad Z = \int_\lambda P(\lambda)\bar{\varepsilon}(\lambda) d\lambda,$$  

where $\lambda$ is the wavelength of the equivalent monochromatic light. $P(\lambda)$ is the spectral power distribution, which is the input for tristimulus values and its data are shown in Fig. 6. $\bar{\varepsilon}(\lambda)$, $\bar{\gamma}(\lambda)$, and $\bar{\varepsilon}(\lambda)$ are the three color-matching functions.

Color temperature ($T_c$) is also a key technical factor for evaluating the applicability of a luminescence material. It can be estimated using McCamy’s equation

$$T_c = 449n^3 + 3525n^2 + 6823.3n + 5520.33,$$

where $n = \frac{0.23881R + 0.2549G + (-0.58291)B}{0.11109R + (-0.85406)G + (0.52289)B}$,  

where $R$, $G$, and $B$ are the spectral matching stimulus which can be calculated by Matrix

$$\begin{pmatrix} X \\ Y \\ Z \end{pmatrix} = \begin{pmatrix} -0.14282 & 1.54924 & -0.95641 \\ -0.32466 & 1.57837 & -0.73191 \\ -0.68202 & 0.77073 & 0.56332 \end{pmatrix} \begin{pmatrix} R \\ G \\ B \end{pmatrix},$$  

where $X$, $Y$, and $Z$ are three tristimulus values which can be calculated as per Eqs. (2) and (3).

The color render index ($R_a$) and color quality scale ($Q_a$) are widely used for assessing the luminescence performance of a light source. Thus, introduction of these parameters is good for investigating the luminescence performance of the samples’ TE$i$ ($i = 0–4$). Detailed procedures for the calculation of $R_a$ and $Q_a$ are available in Refs. [17,18]. The final calculations for these are provided as follows

$$R_a = \frac{1}{8} \sum_{i=1}^{8} (100 - 4.6 \Delta E_i),$$  

where $\Delta E_i$ is the difference in color appearance for each sample between illumination by the test source and the reference illuminant which can be computed in Commission Internationale de L’Eclairage (CIE) $W^sU^sV^s$ uniform color space

$$Q_a = 10 \ln(\exp((100 - 3.1 \times \Delta E_{rms})/10) + 1),$$  

where $\Delta E_{rms}$ is the rms of the 15 color differences for each sample illuminated by the test source and reference illuminant. Note that the $Q_a$ can be calculated by using Eq. (7) when the correlated color temperature of the test light source is greater than 3500 K.

The chromaticity coordinates of the TE$i$ ($i = 0–4$) under 384 nm excitation were calculated using Eq. (2) and are marked in a chromaticity diagram as shown in Fig. 7. It can be seen that emission intensities of the samples are all in the white light region, and the emission of Sample TE4 is much closer to the standard equal energy white light illumination ($x = 0.333$, $y = 0.333$). To further understand the luminous characteristic of these samples, the luminous parameters, including chromaticity coordinates, color temperature ($T_c$), color rendering index ($R_a$), and color quality scale ($Q_a$), which were calculated using Eqs. (2)–(7), are listed in Table 2. Although the luminous properties of these samples fall into the white light region, more effort should focus on decreasing the color and rendering of these samples.
temperature and increase the color quality scale of \( \text{Tb}^{3+}/\text{Eu}^{3+} \) co-doped \( \text{LiYF}_4 \) crystals, which is relegated to future work.

In conclusion, \( \text{LiYF}_4 \) single crystals co-doped with \( \text{Tb}^{3+}/\text{Eu}^{3+} \) for LEDs are obtained by a modified Bridgman method. It shows better luminescent properties from the emission spectra including synchronously blue, green, and red light bands. This work proves that white light emission from \( \text{LiYF}_4 \) crystals co-doped with \( \text{Tb}^{3+}/\text{Eu}^{3+} \) ions can be achieved under a proper excitation wavelength. Furthermore, all the results indicate that the emission light color can be tuned for different demands by varying the excitation wavelengths or adjusting the concentrations of \( \text{Tb}^{3+}/\text{Eu}^{3+} \) ions in \( \text{LiYF}_4 \) single crystals. Due to excellent advantages of white light-emitting crystals, \( \text{LiYF}_4 \) crystals co-doped with \( \text{Tb}^{3+}/\text{Eu}^{3+} \) ions might have broad application prospects for white light emission.

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### References