Photoluminescence Properties and Energy Transfers in the Novel LiYMgWO₆: Dy³⁺, Tm³⁺

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A series of Dy³⁺/Tm³⁺ single doped and co-doped double perovskite-structure compound LiYMgWO₆ (LYMW) are prepared by a solid-state route. The structure and photoluminescence properties have been unraveled by combining experiments and first-principles calculations. The crystal structure was determined to be a monoclinic structure with space groups P2₁. Under the ultraviolet (UV) excitation, Dy³⁺ and Tm³⁺ single doped LYMW samples emit yellowish-white and blue light, respectively. For Dy³⁺ and Tm³⁺ co-doped LYMW, the emission can be tuned from blue to white light and eventually to yellow through energy transfers by varying the Dy³⁺ and Tm³⁺ concentrations. The sample with 3% Dy³⁺ and 3% Tm³⁺ has chromaticity coordinates (0.3405, 0.3378), which are nearest to the ideal white light (0.33,0.33). The energy transfer mechanism is verified to be the quadrupole-quadrupole interaction. The temperature-dependent photoluminescence (PL) spectra show that LYMW: Dy³⁺, Tm³⁺ exhibits good thermal stability.

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Rare earth (RE) doped phosphors are extensively employed as luminescent materials in many fields of applied and fundamental research, such as display, lighting, and detection. Searching for suitable RE dopants with effect absorption is essential and promising to obtain sufficient emitting components in relation to different application scenarios. Dy³⁺ is a popular emitting center for adjusting the color in phosphor because its ⁴F₀→⁴H₁₂₁₂ and ⁴F₀→⁴H₁₅₂ transitions can produce blue and yellow emissions. However, Dy³⁺ activated phosphors suffer from insufficient absorption due to the f-f transitions. Tm³⁺ often shows blue emission peaked at about 457 nm, which has a spectral overlap with the Dy³⁺ excitation, indicating the possibility of the Tm³⁺ → Dy³⁺ energy transfer (ET). That is, co-doping Tm³⁺ would enhance the Dy³⁺ emission intensity.

In addition, hosts with low phonon energy, high chemical stability, and adjustable chemical composition are desirable for high-performance phosphors. In recent years, double perovskite-structure compounds with a formula of A₂B₅O₁₇ (A=Li, Na; B=P, As) have been extensively investigated as phosphor hosts. Except for the common advantages of perovskite-structure compounds such as excellent chemical stability and adjustable chemical composition, A₂B₅O₁₇ compounds possess unique optical properties, such as a broad and strong W⁶⁺/Mo⁶⁺→O²⁻ charge transfer band (CTB) which is often observed in their excitation spectra. Moreover, the A₂B₅O₁₇ compounds allow a high doping level for the rare-earth ions, indicating that a strong emission can be achieved. Plenty of Eu³⁺/Pr³⁺/Sm³⁺ doped A₂B₅O₁₇O₆ have been explored. LiYMgWO₆ (LYMW) is a member of the A₂B₅O₁₇ structure family. Up to now, there is only one report about LiYMgWO₆:Er³⁺, which mainly focuses on the up-conversion chromaticity modulation and applications in the anti-counterfeiting field. To the best of our knowledge, Dy³⁺-activated LiYMgWO₆ has not been reported yet.

In this work, a series of LiYMgWO₆:Dy³⁺/Tm³⁺ samples are prepared and the luminescence properties are discussed for the first time. Tm³⁺ is introduced to LYMW: Dy³⁺ to sensitize Dy³⁺ and boost strong and tunable emissions by employing the ET process. The phase structure, morphology, optical properties, and thermal stability were investigated. The results of this work shed some light on the design and development of Dy³⁺, Tm³⁺ co-doped phosphor. The color-adjustable properties of this series of samples indicate the possibility of further research in this direction. At the same time, our work provides a new strategy for designing novel double perovskite tungstate phosphors with excellent luminescent properties.

Experimental

Materials and preparation.—A series of Dy³⁺/Tm³⁺ singly and co-doped LYMW samples were synthesized via a conventional solid-state reaction. The stoichiometric Li₂CO₃ (99.99%, Aladdin), Y₂O₃ (99.99%, Jiangxi Rare Earth), MgO [4 N], Sinopharm], WO₃ ([A.R., Sinopharm], Dy₂O₃ (99.9%, Hunan Rare Earth) and Tm₂O₃ (99.99%, Hunan Rare Earth) were homogeneously mixed and finely ground in an agate mortar according to the following reaction:

\[
\frac{1}{2} Li_2CO_3 + \frac{1-x-y}{2} Y_2O_3 + MgO + WO_3 + \frac{x}{2} Dy_2O_3 + \frac{y}{2} Tm_2O_3 \rightarrow LiY_{1-x-y}Dy_xTm_yMgWO_6 + \frac{1}{2} CO_2
\]

Then, the mixture was packed in aluminum oxide crucibles and preheated in a muffle furnace at 600 °C for 3 h. After that, the mixture was sintered in a high-temperature tube furnace at 900 °C for 6 h. All the experimental processes were completed in an air environment. At last, the samples were ground into proper size powders after natural cooling for further characterization.

Characterization

The X-ray diffraction (XRD) patterns of the products were obtained by using a D8 advance X-ray diffractometer with a Cu Ko X-ray tube. Crystal structure Rietveld refinements were performed by the General Structure Analysis System (GSAS) software suite. The morphology of the sample was investigated using a scanning electron microscope (SEM, FEI Apero S, USA). The diffuse reflection spectrum was measured with a UV–vis spectrophotometer (Shimadzu UV-2600) in the range of 200 ~ 700 nm. A Zolix spectrophotometer with a 150 W xenon lamp was applied to collect the room temperature photoluminescence (PL) and photoluminescence excitation (PLE) spectra. The temperature-dependent
luminescence properties were measured on the same spectrophotometer, which was combined with a self-made heating attachment. By exciting the samples with a supercontinuum white light laser (SuperK EVO, NKT Photonics), the PL decay curves were detected by an Edinburgh Instruments system (LifeSpec II).

**Computational methods.**—The density functional theory (DFT) calculations were carried out using the generalized density approximation (GGA)-Perdew–Burke–Ernzerhof (PBE) functional for relaxation of the atomic positions and calculation of the equilibrium cell volumes. The projector augmented wavefunction (PAW) approach as implemented in the Vienna Ab initio Simulation Package (VASP) was used for the description of electronic wave functions. An energy cutoff of plane-wave expansion was 450 eV and the Brillouin zone integration was represented using the K-point sampling scheme of 5*5*3 Monkhorst-Pack scheme. The total energy and geometry relaxation are calculated by using Gaussian smearing. The structural relaxation calculations were performed using the conjugate gradient technique where the energy change was less than $10^{-6}$ eV and the Hellmann Feynman forces on atoms were less than 0.01 eV Å$^{-1}$. After the atomic positions were fully relaxed by using DFT, the equilibrium cell volumes were determined by fitting the total energies of the supercell varying in the volume interval ($\Delta V_0 \pm 7\%$) to the Birch-Murnaghan equation of state.

**Results and Discussion**

**Structure and photoluminescence properties of LYMW host.**—Figure 1a depicts the view of the LYMW unit cell. Li$^+$ and Y$^{3+}$ possess a layered ordering. Mg$^{2+}$ and W$^{6+}$ possess a rock-salt ordering. This is consistent with the typical A$_i$A$_{ii}$Bi(W/Mo)O$_6$ double perovskite-structure compounds. When RE$^{3+}$ is doped into the host lattice, it will preferentially enter the Y$^{3+}$ site given the similar valence state and ionic radius. In LYMW, only one type of Y$^{3+}$ crystallographic site coordinated by eight oxygen atoms is found. There are three types of Y$^{3+}$–O$_2^-$ bond lengths, so it possesses a non-inversion symmetry environment. According to previous reports, when Dy$^{3+}$ occupies a low symmetry site, the transition intensity of $^7F_{0/2} \rightarrow ^5H_{3/2}$ will be higher than that of $^7F_{0/2} \rightarrow ^5H_{15/2}$, and a yellowish-white emission will be brought out. Thus, a yellowish-white emission can be predicted in LYMW: Dy$^{3+}$. What is more, the special layered arrangement of Y$^{3+}$ would facilitate the high contents of the luminescence centers in the host.

The SEM image in Fig. 1b shows the crystalline morphology of the LYMW host. The powders are well crystallized with irregular particle shapes, and an agglomerated phenomenon for the powders is observed from the image. The main powders are in micrometer size of 3–5 μm, which is suitable to apply as phosphors. To the best of our knowledge, the detailed information for the LYMW crystal structure has not been reported yet. The XRD pattern of the as-prepared LYMW powders is illustrated in Fig. 1c, which matches well with that of monoclinic NaYMgWO$_6$ with space groups P2$_1$ in the previous report. However, the peak splitting is much more obvious in the LYMW sample, which may be a result of the reduced symmetry due to the replacement of the relatively larger Na$^+$ by the smaller Li$^+$. To obtain the basic electronic properties of the LYMW host, the first-principles calculations are employed in this work. Table I shows the DFT calculated and experimental lattice parameters of pure LYMW. They match well with each other (the maximum difference is only 1.0%), confirming the rationality of the adopted NaYMgWO$_6$ structure model. The calculated band structure, total density of states (TDOS), and projected density of states (PDOS) of LYMW based on GGA-PBE functional are depicted in Figs. 2a and 2b. Both the valence band maximum (VBM) and the conduction band minimum (CBM) are located at the same high symmetry point Γ, indicating a direct band transition. The band structure of the host LYMW consists of 1) The quite narrow and deep state of Y$^{3+}$ at about $-20$ eV; 2) The $t_2$ band of O 2$s$ with some contribution of W 5$d$; 3) the valence band (VB) from $-7$ eV to the Fermi level; 4) the conduction band (CB) between 4 eV to 12 eV. The W 5$d$ states can

\[ \text{Figure 1. (a) Structure view of LYMW and local coordination surroundings of Y}^{3+} \text{ ion. (b) SEM image of LYMW host. (c) XRD patterns of LYMW and NaYMgWO}_6. \]
be divided into occupied ones and unoccupied ones, the occupied ones accommodate 4 electrons (5d⁴) and the unoccupied ones correspond to 6 electrons. The bonds between W and O, Mg and O form a wide band starting from the Fermi level, i.e., the VB is mainly contributed by the O 2p, W 5d, and Mg 3s. The non-bonding valence electrons of O, residing as lone electron pairs, form states at the edge of the VB at 0 eV (i.e., VBM). The CBM is mainly composed of W 5d states. The calculated band-gap is 3.71 eV, which is within the band-gap demand of 3.0 ∼ 6.0 eV for the matrix. That is to say, LYMW has a wide enough band gap, which can accommodate both ground and excited states of luminescent centers within the band-gap, and should be a potential phosphor host.

The diffuse reflectance spectrum (DRS) of the LYMW host is shown in Fig. 2c. The sample exhibits a strong reflection within the entire visible light range. It starts to fall at ~400 nm and reaches a minimum at ~290 nm, which indicates an appearance of a broad absorption band within this wavelength. From the calculated PDOS results, this band can be assigned to O²⁻ → W⁶⁺ CTB. Based on the DRS, the LYMW powders are not doubting appeared as a white color under natural light, just as shown in the inset of Fig. 2c. The band-gap (E_g) can be estimated based on the data of DRS according to the following equation:

\[(ahv)^n = A(hv - E_g),\]  

where \(hv\) is the incident photon energy, \(\alpha\) is the absorption coefficient, and \(A\) is a constant. The value of \(n\) depends on the type of the interband transition: that is \(n = 2\) for direct transition and \(n = 1/2\) for indirect transition.²⁶ LYMW is a direct transition compound, i.e., \(n = 2\), and the estimated band-gap from the DRS is about 3.91 eV, which is very close to the calculated result (3.71 eV). The slight discrepancy between the calculated band-gap and the experimental one is due to the inherent flaw of DFT calculations with the GGA-PBE functional.²⁷

Table I. The experimental and DFT calculated structural parameters of pure LYMW.

|       | a (Å) | b (Å) | c (Å) | α  =  β | V (Å³) |
|-------|------|------|------|------|--------|
| Cal.  | 5.319| 5.568| 7.762| 90°   | 90.07° | 229.9  |
| Exp.  | 5.299| 5.510| 7.705| 90°   | 90.12° | 224.9  |

Figure 2d shows the PL and PLE spectra of the undoped LYMW. A broad excitation band ranging from 250 to 350 nm with a maximum of 290 nm is detected in the excitation spectrum of LYMW when monitored at the emission peak of 440 nm. This matches well with the DRS spectrum and the DFT calculation results. The emission spectrum under the maximum excitation of 290 nm shows a broad blue emission band peaking at ~440 nm. The digital photo of LYMW powder upon UV excitation of 254 nm is displayed in Fig. 2d, a relatively weak blue emission can be seen with naked eyes.

Structure and luminescent properties of LYMW: Dy³⁺.—The XRD patterns of the LYMW: xDy³⁺ (x = 0%, 2%, 4%, 6%, 8%, 10%) samples are shown in Fig. 3. All diffraction peaks can be well indexed as pure crystalline LYMW, which confirms the samples are single-phase NaYMgWO₆ isostructure. The introduction of Dy³⁺ dopant into the host does not take any significant change to the diffraction peaks. From the enlarged image of the spectra range of 32° to 35°, it is observed that the diffraction peaks slightly shift to the small angle side with increasing Dy³⁺ concentration \(x\). This can be attributed to the enlarging of lattice constants as the substitution of \(Y^{3+}\) ion (CN = 8, \(R_{Y^{3+}} = 1.019\) Å) by a little bigger \(Dy^{3+}\) ion (CN = 8, \(R_{Dy^{3+}} = 1.027\) Å).

Figure 4a shows the PLE spectra of LYMW: \(x\)Dy³⁺ (\(x = 2\%, 4\%, 6\%, 8\%, 10\%) samples monitored at their peak emission of

Figure 2. (a) Band structure and (b) the TDOS and PDOS of LYMW calculated by the PBE functional. (c) Diffuse reflectance spectra (Insert: the corresponding Tauc plots curves) and (d) PL and PLE spectra of the LYMW sample. The digital photos of the LYMW powders upon daylight and UV lamp are also shown in the inset of (c) and (d), respectively.
∼575 nm. All the spectra exhibit a similar profile, and they are composed of several excitation bands. The one within 225 ∼ 320 nm is assigned to the CTB of $\text{O}^{2-} \rightarrow W^{6+}$, which is consistent with the undoped LYMW in Fig. 2d. The other excitation bands located at 325 nm, 352 nm, 367 nm, and 387 nm could be assigned to the $^4\text{H}_{15/2} \rightarrow ^4\text{P}_{9/2}$, $^4\text{H}_{15/2} \rightarrow ^4\text{P}_{7/2}$, $^4\text{H}_{15/2} \rightarrow ^4\text{P}_{5/2}$ and $^4\text{H}_{15/2} \rightarrow ^4\text{F}_{7/2}$ transitions of Dy$^{3+}$, respectively. The intensity of all the excitation bands of the PLE spectra exhibits the same trend with increasing concentration.

Figure 3. (a) XRD patterns and (b) their enlarged profile within the range of 32° ∼ 35° of LYMW: $x$Dy$^{3+}$ ($x = 0\%$, 2\%, 4\%, 6\%, 8\%, 10\%) samples.

Figure 4. (a) PLE and (b)-(c) PL spectra of LYMW: $x$Dy$^{3+}$ ($x = 0\%$, 2\%, 4\%, 6\%, 8\%, 10\%) samples (Inset: CIE chromaticity diagram for the LYMW: 6\%Dy$^{3+}$ phosphor). (d) Dependence of peak intensity of Dy$^{3+}$ emission with its concentration $x$. (Inset: the relationship of $\ln(I/I_D)$ vs $\ln(1-x_D)$).
Dy$^{3+}$ concentration, i.e., it increases at first, reaches the maximum at $x = 6\%$, and then starts to decrease. The highest and the second-highest PLE spectrum peaks (290 nm and 352 nm) are chosen as the excitation sources to detect the PL spectra, see Figs. 4b and 4c. It is obvious that under the same excitation source, the PL spectra have a similar shape, but their intensities are quite different as the Dy$^{3+}$ concentration $x$ varies. When the samples are excited by a 352 nm light source, their PL spectra are comprised of a weak blue emission band peaking at 484 nm, a strong yellow one peaking at 575 nm, and a much weaker red one peaking at 660 nm. These three bands can be attributed to the $^{4}F_{9/2} \rightarrow ^{4}I_{15/2}, ^{4}F_{9/2} \rightarrow ^{4}I_{13/2},$ and $^{4}I_{15/2} \rightarrow ^{4}I_{11/2}$ transitions of Dy$^{3+}$, respectively. When the samples are excited by a 290 nm light source, in the PL spectra the sides three bands deriving from Dy$^{3+}$, there is an additional weak broadband due to the LYMW host. The intensity of the three Dy$^{3+}$-related bands, it shows that the blue band is weaker than the yellow one, indicating that the Dy$^{3+}$ should occupy at the low symmetry site in the LYMW host. A yellowish-white emission with coordinates of (0.4053,0.4398) is observed in the CIE chromaticity diagram for the representative LYMW: 6% Dy$^{3+}$ sample excited by a 352 nm light source.

Interestingly, the intensity of the PL spectra in Figs. 4b and 4c exhibits the same Dy$^{3+}$ concentration $x$ dependency as that of the PLE spectra, i.e., it increases at first, reaches the maximum at $x = 6\%$, and then decreases as a result of concentration quenching effect, see Fig. 4d. According to L. Ozawa’s theory, the quenching concentration can be estimated by $1/(1 + z)$, wherein $z$ represents the number of closest cations around the emitting center. The value of $z$ can be obtained by the equation

$$\ln\left(\frac{I}{x}\right) = Z \ln(1 - x) + C, \quad [2]$$

where $I$, $x$, and $C$ are the luminescence intensity, the concentration, and a constant, respectively. Based on the experimental data, the relationship of $\ln(I/ax) \sim \ln(1-xp)$ for LYMW: $x$ Dy$^{3+}$ is displayed in the insert of Fig. 4d. The slope $Z$ is determined to be 15.7228, thereby the quenching concentration is calculated to be 5.98%, which is much closer to the direct experimental result of $x = 6\%$. Thus, it is concluded that the optimal concentration of Dy$^{3+}$ in LYMW: $x$ Dy$^{3+}$ is 6\%.

**Structure and luminescent properties of LYMW: $x$ Dy$^{3+}$ phosphors.** The above discussion shows that the Dy$^{3+}$ ion single-doped phosphors LYMW: $x$ Dy$^{3+}$ generate a yellowish-white emission while excited by UV light sources. This yellowish-white emission is deviated from the ideal white light due to the lack of blue emission components. One possible solution is to introduce the rare earth ion Tm$^{3+}$ to LYMW: $x$ Dy$^{3+}$ samples, because the Tm$^{3+}$ ion usually acts as a blue luminescent center in phosphors. To validate this solution, we first investigated the structure and luminescent properties of Tm$^{3+}$ ion single-doped phosphors LYMW: $y$ Tm$^{3+}$.

Powder XRD patterns of LYMW: $y$ Tm$^{3+}$ ($y = 0\%, 0.1\%, 0.5\%, 1\%, 2\%, 3\%, 4\%, 6\%,$ and $10\%$) samples are illustrated in Fig. 5. All the diffraction peaks match well with the pure LYMW host, i.e., a single-phase isostructure of NaYMGWO$_4$ is obtained. From the enlarged profiles within $32\textdegree$-$35\textdegree$, the Tm$^{3+}$ ion concentration $y$ increases from 0.1% to 3%, the diffraction peaks shift to the large angle side, but the peaks move toward the opposite angle direction beyond $y = 3\%$. The movement to the large angle side when $y < 3\%$ can be well and easily interpreted by the Bragg equation, because the big $V^{1+}$ ($CN = 8, R_{pA^{3+}} = 1.019 \text{Å}$) is replaced by small Tm$^{3+}$ ($CN = 8, R_{pA^{3+}} = 0.994 \text{Å}$). The abnormal movement to the small angle side when $y > 3\%$ may be due to the minor non-equivalent substitution of divalent Mg$^{2+}$ or mono-valence Li$^{1+}$ by trivalent Tm$^{3+}$, which leads to an expansion of the lattice.

Figures 6a and 6b show the $y$ dependent PLE spectra of LYMW: $y$ Tm$^{3+}$ ($y = 0\%, 0.1\%, 0.5\%, 1\%, 2\%, 3\%, 4\%, 6\%,$ and $10\%$) samples monitored at 455 nm and 475 nm, respectively. The PLE spectrum of pure LYMW: $y$ Tm$^{3+}$ ($y = 0\%)$ is also presented for comparison. All the PLE spectra consist of a broad excitation band in the range of 250 $\rightarrow$ 350 nm with a maximum at 290 nm, which is ascribed to the CTB of O$^{2-} \rightarrow$ W$^{6+}$, indicating the possibility of energy transfer from the host to Tm$^{3+}$. For the emission at 455 nm, a sharp peak located at ~360 nm is observed in the PLE spectra as compared to that of pure LYMW: $y$ Tm$^{3+}$ ($y = 0\%)$. This sharp peak derives from the $^{3}H_{4} \rightarrow ^{1}D_{2}$ transition of Tm$^{3+}$.

In Figs. 6c and 6d, both the excitation peaks of CTB of O$^{2-} \rightarrow$ W$^{6+}$ ($\lambda_{ex} = 290$ nm) and Tm$^{3+}$-related band ($\lambda_{ex} = 355$ nm) are chosen as the excitation sources to investigate the PL spectra of the samples. For the 290 nm excitation source cases, a broad and indistinguishable PL band is observed for all $y (0\%)$ samples, because both the LYMW host and Tm$^{3+}$ are excited simultaneously. The emission intensity increases firstly and then decreases with the Tm$^{3+}$ concentration increasing. The best Tm$^{3+}$ concentration for the 475 nm emission peak is only 1%, because this peak is attributed to the $^{1}G_{4} \rightarrow ^{3}H_{4}$ transitions of Tm$^{3+}$, and it could only be activated by the energy transfer between the host and Tm$^{3+}$, which is also confirmed by the PLE spectra in Fig. 6b.

When the samples are excited by a 358 nm light source, only Tm$^{3+}$ is excited, i.e., the excitation of the LYMW host is absent at this wavelength. In all the PL spectra, there is a strong emission peak at 455 nm and a weak emission peak at about 475 nm, which originated from Tm$^{3+}$, $^{1}D_{2} \rightarrow ^{3}F_{4}$ and $^{1}G_{4} \rightarrow ^{3}H_{4}$ transitions, respectively. These two emission bands mix into blue photoluminescence with chromaticity coordinates (0.1545, 0.0413) when $y = 4\%$, see the inset of Fig. 6d. The intensity increases at first and reaches the maximum at $y = 4\%$. Then, it decreases when $y > 4\%$ due to the concentration quenching effect. Therefore, the best doping concentration of Tm$^{3+}$ in LYMW is 4%, when the samples are excited by a 358 nm light source. No matter under the UV (290 nm) or NUV (358 nm) excitation, a blue emission can be obtained by doping Tm$^{3+}$ into the LYMW host.

**Luminescent properties and energy transfer of LYMW: $y$ Dy$^{3+}, Tm^{3+}$.** The CIE chromaticity coordinates of LYMW: $y$ Tm$^{3+}$ and LYMW: $y$ Dy$^{3+}$ samples are shown in Fig. S1 (available online at stacks.iop.org/ECSA/1/025001/mmedia). The coordinate of LYMW: $Tm^{3+}$ is located in the blue region. Interestingly, the ideal white light coordinates (0.33, 0.33) are on the straight line which connects the coordinates of LYMW: $Tm^{3+}$ and LYMW: $Dy^{3+}$, indicating that the emission light can be modulated to white light by co-doping LYMW with $Dy^{3+}$ and $Tm^{3+}$. The top of Fig. 7 shows the digital photos of three grooves of “Department,” “of” and “Physics” respectively filled with LYMW: 6% Dy$^{3+}$, LYMW: 4% Tm$^{3+}$ and LYMW: 3% Dy$^{3+}$, 3% Tm$^{3+}$ phosphors under daylight and UV lamp excitation. It is intuitive to show the effect of doing Tm$^{3+}$ as a complement to the blue component of the LYMW: Dy$^{3+}$ phosphor, and improve the white light. To obtain ideal white light, we synthesized LYMW: $Dy^{3+}, Tm^{3+}$ samples of various Dy$^{3+}$ and Tm$^{3+}$ concentrations, see Fig. 7. The digital photos show that the emission colors of the phosphors can be tuned from blue through white light and eventually to yellow by systematically adjusting the Dy$^{3+}$ and Tm$^{3+}$ dopant concentrations. From the calculations of their CIE chromaticity coordinates, it reveals that the sample with 3% Dy$^{3+}$ and 3% Tm$^{3+}$ co-doped has chromaticity coordinates of (0.3405, 0.3378), which are quite close to the ideal white light (0.33,0.33) and the CCT can also be calculated to be 5145 K, see Fig. S1. We focus on the doping concentration of 3% for both Dy$^{3+}$ and Tm$^{3+}$ in the following work.

XRD patterns of the two series samples LYMW: $y$ Dy$^{3+}, 3% Tm^{3+}$ ($y = 1 \sim 5\%$) and LYMW: $3% Dy^{3+}, y$ Tm$^{3+}$ ($y = 1 \sim 5\%$) are shown in Figs. S2 and S3. All the diffraction peaks of these samples are consistent with those of pure LYMW without any detectable additional peaks, indicating that the co-dopants $Tm^{3+}$ and Dy$^{3+}$ samples are successfully incorporated into the LYMW host. The Energy-Dispersive X-ray Spectroscopy (EDS) and elemental composition percentage of LYMW: 3% Dy$^{3+}$, 3% Tm$^{3+}$ are exhibited in Fig. S4. The result of EDS shows that the main elemental...
components present in the samples are Y, Mg, W, O, Dy and Tm. It is worth mentioning that the Li signal is not detected due to its very low energy of characteristic radiation. The molar ratio of Y, Mg, W, and O is approximately 1:1:1:7 as shown in Fig. S4b, which consists of the original composition of the materials. As can be seen in Figs. S4c–S4h, Y, Mg, W, O, Dy and Tm elements are evenly distributed throughout the samples. This analysis further confirms that the Dy$^{3+}$ and Tm$^{3+}$ are successfully doped into the host. The emission color variation of Dy$^{3+}$ and Tm$^{3+}$ co-doped LYMW as changing the Dy$^{3+}$ and Tm$^{3+}$ dopant concentrations might be a result of the energy transfer. In most Dy$^{3+}$ and Tm$^{3+}$ co-doped phosphors, the emission spectrum of Tm$^{3+}$ usually overlaps with the excitation spectrum of Dy$^{3+}$. There would be an energy transfer between Tm$^{3+}$ and Dy$^{3+}$, i.e., Tm$^{3+}$ plays as a sensitizer, while Dy$^{3+}$ works as an activator. To verify the possibility and reasonability of energy transfer between Tm$^{3+}$ and Dy$^{3+}$ in our co-doped samples, the PL spectrum of LYMW: 4%Tm$^{3+}$ and the PLE spectrum of LYMW: 6%Dy$^{3+}$ are depicted in Fig. S5. A remarkable spectral overlapping within the range of 450 ~ 500 nm is observed, i.e., Tm$^{3+}$–Dy$^{3+}$ co-doped samples may emit white light via energy transfer between Tm$^{3+}$ and Dy$^{3+}$.

The PL spectra and the corresponding emission peak intensity of LYMW: xDy$^{3+}$, yTm$^{3+}$ (x, y = 1 ~ 5%) are illustrated in Fig. 8. Under the excitation of a 358 nm light source, the PL spectra are comprised of the emission bands of Tm$^{3+}$ and Dy$^{3+}$, which are the same as those of Dy$^{3+}$ and Tm$^{3+}$ single-doped LYMW. In Figs. 8a and 8b, for a fixed Tm$^{3+}$ concentration (y = 3%) and a varying Dy$^{3+}$ concentration x, the emission intensity of Tm$^{3+}$ (represented by 455 nm) decreased monotonically with increasing x, indicating the occurrence of the Tm$^{3+}$ → Dy$^{3+}$ energy transfer. At the same time, in Figs. 8c and 8d, for a fixed Dy$^{3+}$ concentration (x = 3%), the emission intensity of Dy$^{3+}$ is enhanced with increasing Tm$^{3+}$ concentration y, further confirming the Tm$^{3+}$ → Dy$^{3+}$ energy transfer process in LYMW: Dy$^{3+}$, Tm$^{3+}$ samples. In Figs. 8b and 8d, the emission peak intensities of Dy$^{3+}$ (Tm$^{3+}$) reach the maximum at x (y) = 3%, and then start to decrease although the doping concentration x (y) is kept increasing. This decline is a result of the concentration quenching effect; however, it is worth noting that the sum of x and y (x + y = 0.6) for the quenching point is equal to that of the single-doped Dy$^{3+}$ sample, indicating that the decreased quenching concentration maybe results from both Tm$^{3+}$ and Dy$^{3+}$ competitively occupying the Y$^{3+}$ sites.
To figure out the process of the $\text{Tm}^{3+} \rightarrow \text{Dy}^{3+}$ energy transfer in $\text{Tm}^{3+}$ and $\text{Dy}^{3+}$ co-doped LYMW, the schematic energy-level diagram of $\text{Tm}^{3+}$ and $\text{Dy}^{3+}$ is illustrated in Fig. S6. Upon 358 nm light excitation, the electrons of $\text{Tm}^{3+}$ at the ground level $^3\text{H}_6$ can be inspired to the excited $^1\text{D}_2$ level, after which a blue emission at 455 nm originating from $^1\text{D}_2 \rightarrow ^3\text{F}_4$ radiation transition can be observed in LYMW: $\text{yTm}^{3+}$ ($\text{y} = 0\%, 0.1\%, 0.5\%, 1\%, 2\%, 3\%, 4\%, 6\%, 8\%, 10\%$) phosphors (Inset: CIE chromaticity diagram for the LYMW: 4\%$\text{Tm}^{3+}$ phosphor).

The decay curves of $\text{Tm}^{3+}$ emission at $\lambda_{\text{em}} = 455$ nm with $\lambda_{\text{ex}} = 358$ nm in LYMW: $\text{yDy}^{3+}, 3\%\text{Tm}^{3+}$ are investigated, as shown in Fig. 9a. The average lifetime $\tau$ can be calculated by the equation

$$\tau = \int_0^\infty \frac{t \times I(t) dt}{\int_0^\infty I(t) dt},$$

where $I(t)$ is the luminous intensity at time $t$. They are found to be 7.58 $\mu$s, 7.28 $\mu$s, 6.69 $\mu$s, 6.11 $\mu$s, and 5.77 $\mu$s for the samples with $x = 1\%, 2\%, 3\%, 4\%$, and 5\%, respectively. It shows that the average lifetime $\tau$ decreases as the $\text{Dy}^{3+}$ concentration $x$ increases, which is another powerful evidence for $\text{Tm}^{3+} \rightarrow \text{Dy}^{3+}$ energy transfer. The energy transfer efficiency $\eta$ can be obtained by

$$\eta = 1 - \frac{\tau}{\tau_0},$$

where $\tau_0$ and $\tau_0$ represent the lifetime of the sensitizer $\text{Tm}^{3+}$ with and without the activator $\text{Dy}^{3+}$. As illustrated in Fig. 9b, the energy transfer efficiency $\eta$ increases monotonically along with elevated $\text{Dy}^{3+}$ concentration. Compared with many other phosphors, LYMW: 3\%$\text{Dy}^{3+}, 3\%\text{Tm}^{3+}$ phosphor shows a well PL quantum yield ($\sim 59.7\%$), see Table II and Fig. S7.

The energy transfer mechanism can be either multipolar interaction or exchange interaction. If the critical distance ($R_C$) between the sensitizer and the activator is smaller than 5 Å, and there is a large overlap between the PL spectrum of the sensitizer and the PLE spectrum of the activator, the energy transfer should be due to the
exchange interaction, otherwise, the multipolar interaction will dominate the energy transfer process. The critical distance $R_C$ can be obtained by:

$$ R_C \approx \left( \frac{3V}{4\pi X_C Z} \right)^{\frac{1}{3}}. $$

where $X_C$ is the critical concentration, $Z$ is the number of sites in the unit cell for the dopants, and $V$ is the volume of the unit cell. For LYMW: Dy$^{3+}$, Tm$^{3+}$ samples, $X_C = 6\%$, $Z = 4$, and $V = 224.935$, thus $R_C$ is determined to be 12.13 Å, which is much bigger than 5 Å. Therefore, the energy transfer from Tm$^{3+}$ to Dy$^{3+}$ in LYMW is ascribed to the multipolar interaction. According to the energy transfer theory of Dexter and Reisfeld, the specific type of multipolar interaction is determined by using the relation:

$$ I_{0i} \propto C_i^3, $$

Table II. Comparison of quantum yield of LYMW: 3% Dy, 3% Tm with other co-doped phosphors.

| Phosphor                     | Quantum yield (%) | References |
|------------------------------|-------------------|------------|
| LiYMgWO$_4$:Dy$^{3+}$, Tm$^{3+}$ | 59.7%             | This work  |
| Ca$_2$MgLu (PO$_4$)$_2$:Dy$^{3+}$, Tm$^{3+}$ | 29%             | 33         |
| Ca$_2$MgLu (PO$_4$)$_2$:Ce$^{3+}$, Tb$^{3+}$ | 68%             | 34         |
| Ba$_2$Y$_2$Si$_2$O$_8$:Tm$^{3+}$, Dy$^{3+}$ | 40.86%             | 35         |
| Y$_2$GeO$_5$:Bi$^{3+}$, Eu$^{3+}$ | 37.4%             | 36         |
| KAlSiO$_4$:Sm$^{3+}$, Eu$^{3+}$ | 51%             | 37         |

Figure 8. (a) The PL spectra and (b) the corresponding emission peak intensity of LYMW: $x$Dy$^{3+}$, 3%Tm$^{3+}$. (c) The PL spectra and (d) the corresponding emission peak intensity of LYMW: 3%Dy$^{3+}$, $y$Tm$^{3+}$.

Figure 9. (a) Fluorescence decay curves of Tm$^{3+}$ | D$_2$F-$D_4$ for LYMW: Dy$^{3+}$, Tm$^{3+}$ ($\lambda_{ex} = 358$ nm, $\lambda_{em} = 455$ nm). (b) The dependence of the energy transfer efficiency on Dy$^{3+}$ doping concentration.
where \( I_{0} \) and \( I \) denote the emission intensity of \( \text{Tm}^{3+} \) in the absence and presence of \( \text{Dy}^{3+} \). \( C \) is the sum of the concentration of \( \text{Tm}^{3+} \) and \( \text{Dy}^{3+} \), and \( n = 6, 8, \) and 10 means the multipolar interaction ascribed to dipole-dipole, dipole-quadrupole, and quadrupole-quadrupole interaction, respectively. As in Fig. 10, the best liner fitting relationship is obtained at \( n = 10 \), demonstrating that the energy transfer process from \( \text{Tm}^{3+} \) to \( \text{Dy}^{3+} \) in LYMW is realized by the quadrupole-quadrupole interaction.

Thermal stability is one of the crucial properties of phosphors. The PL spectrum of the representative sample LYMW: 3\%\( \text{Dy}^{3+} \), 3\%\( \text{Tm}^{3+} \) excited by 358 nm is collected at the temperature range of 303 °C – 523 K, see Fig. 11. A decline in the emission intensity with increasing temperature is observed due to the thermal quenching effect. As the temperature increased to 473 K, the integrated emission intensity dropped to approximately 60.13% of that at room temperature (303 K). Compared with many other co-doped single-phase white phosphors, LYMW: \( \text{Dy}^{3+} \), \( \text{Tm}^{3+} \) shows a better luminescence performance at high temperatures, see Table III.

**Conclusions**

In summary, a simple solid-state route is adopted to synthesize a series of LYMW: \( \text{Dy}^{3+} \), \( \text{Tm}^{3+} \). The crystal structure and luminescence properties are investigated by combining experiments and DFT calculations. LiYMgWO6: \( \text{Tm}, \text{Dy} \) crystallizes into a monoclinic structure with space groups \( P2_1 \). Under the UV excitation, the \( \text{Dy}^{3+} \) and \( \text{Tm}^{3+} \) single-doped LYMW samples can emit yellowish-white and blue light, respectively. The emission colors of \( \text{Dy}^{3+} \) and \( \text{Tm}^{3+} \) co-doped LYMW could be tuned from blue to white light and eventually to yellow through energy transfers by varying the \( \text{Dy}^{3+} \) and \( \text{Tm}^{3+} \) concentrations. The sample with 3\%\( \text{Dy}^{3+} \) and 3\%\( \text{Tm}^{3+} \) has chromaticity coordinates of (0.3405, 0.3378), which

![Figure 10](image1.png)

**Figure 10.** The relationship between \( I_{0}/I \) of \( \text{Tm}^{3+} \) and \( C_{\text{Tm}, \text{Dy}}^{1/3} \) (a) \( n = 6 \), (b) \( n = 8 \), (c) \( n = 10 \).

![Figure 11](image2.png)

**Figure 11.** Temperature-dependent PL spectra of LYMW: 3\%\( \text{Dy}^{3+} \), 3\%\( \text{Tm}^{3+} \) phosphor under 358 nm excitation, and (b) Normalized emission intensities at different temperatures.

| Phosphor                  | End Temperature | Residual Intensity | References |
|---------------------------|-----------------|--------------------|------------|
| LiYMgWO6: \( \text{Tm}, \text{Dy} \) | 473 K           | 60.13%             | This work  |
| \( \text{K}_{2} \text{Y(WO}_{4})_{2} \cdot \text{PO}_{4} \): \( \text{Tm}, \text{Dy} \) | 473 K           | Less than 60%      | 41         |
| \( \text{LaMgAl}_{11} \text{O}_{19} \): \( \text{Tm}, \text{Dy} \) | 473 K           | Less than 51%      | 42         |
| \( \text{K}_{2} \text{Gd(PO}_{4})_{3} \): \( \text{Tm}, \text{Dy} \) | 473 K           | 45%                | 43         |
| \( \text{NaGd(MO}_{4})_{2} \): \( \text{Dy}, \text{Tm} \) | 473 K           | 60%                | 44         |
| \( \text{Ba}_{5} \text{La}_{2} \text{Si}_{6} \text{O}_{24} \): \( \text{Bi}, \text{Eu} \) | 473 K           | 50%                | 45         |

Table III. Comparison of the thermal stability of LYMW: 3\%\( \text{Dy}, 3\% \text{Tm} \) with other co-doped phosphors.
are nearest to the ideal white light (0.33,0.33). The energy transfer mechanism is verified to be the quadrupole-quadrupole interaction. The temperature-dependent PL spectra demonstrate that LYMW: Dy$^{3+}$, Tm$^{3+}$ has relatively good thermal stability.

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References

1. X.-J. Wang, S. Funahashi, T. Takeda, T. Suehiro, N. Hiroseki, and R.-J. Xie, *J. Mater. Chem. C*, 4, 9968 (2016).
2. Q. Yao, P. Hu, P. Sun, M. Liu, R. Dong, K. Chao, Y. Liu, J. Jiang, and H. Jiang, *Adv. Mater.*, 32, 1907888 (2020).
3. Z. Jia, C. Yuan, Y. Liu, X.-J. Wang, P. Sun, L. Wang, H. Jiang, and J. Jiang, *Light, science & applications*, 9, 86 (2020).
4. P. Huang, W. Zheng, Z. Gong, W. You, J. Wei, and X. Chen, *Materials Today Nano*, 5, 100031 (2019).
5. Z. Wang, J. Chen, Q. Li, and Y. Liu, *Chem. Phys. Lett.*, 771, 138481 (2021).
6. E. A. Rathnakumari and S. M. M. Kennedy, *J. Lumin.*, 235, 118018 (2021).
7. A. R. Kadam, S. B. Dhoble, G. C. Mishra, A. D. Deshmukh, and S. J. Dhoble, *J. Mol. Struct.*, 1235, 13015 (2021).
8. X. Wang, X. P. Li, S. Xu, L. H. Cheng, J. S. Sun, J. S. Zhang, X. Z. Zhang, and B. J. Chen, *Journal of Asian Ceramic Societies*, 8, 1066 (2020).
9. M. C. Knapp and P. M. Woodward, *J. Solid State Chem.*, 179, 1076 (2006).
10. P. M. Woodward, *Acta Crystallogr.*, 53, 32 (1997).
11. S. L. Dong, S. Ye, L. L. Wang, X. Y. Chen, S. B. Yang, Y. J. Zhao, J. G. Wang, X. P. Jing, and Q. Y. Zhang, *Journal of Alloys & Compounds*, 610, 402 (2014).
12. Q. Liu, X. B. Li, B. Zhang, L. X. Wang, Q. T. Zhang, and L. Zhang, *Ceram. Int.*, 42, 15294 (2016).
13. B. Han, Y. Z. Dai, J. Zhang, X. Y. Wang, W. H. Shi, and H. Z. Shi, *J. Lumin.*, 196, 275 (2018).
14. B. Han, Y. Z. Dai, J. Zhang, B. K. Liu, and H. Z. Shi, *Ceram. Int.*, 44, 3734 (2018).
15. W. T. Hu, T. Li, X. Liu, D. Dastan, K. W. Ji, and P. J. Zhao, *Journal of Alloys & Compounds*, 818, 152933 (2020).
16. J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 77, 3865 (1996).
17. G. Kresse and D. Joubert, *Physical Review B*, 59, 1758 (1999).
18. G. Kresse and J. Furthmüller, *Physical Review B*, 54, 11169 (1996).
19. G. Kresse and J. Hafner, *Physical Review B, Condensed matter*, 47, 558 (1993).
20. Q. Yang, G. F. Li, Y. G. Wei, and H. Y. Chai, *J. Lumin.*, 199, 323 (2018).
21. Q. Liu, J. Guo, M. H. Fan, Q. Zhang, S. Liu, K. L. Wong, Z. Y. Liu, and B. Wei, *J. Mater. Chem. C*, 8, 2117 (2020).
22. Q. B. Li, L. Zhang, F. Z. Zhen, S. Wei, W. Bu, Q. Yao, Z. G. Jiang, and H. Chen, *Ceram. Int.*, 44, 15568 (2018).
23. A. R. Shartis, J. F. Khoury, and P. M. Woodward, *Inorg. Chem.*, 55, 12383 (2016).
24. Q. Liu, J. L. Shen, T. Xu, L. X. Wang, J. Zhang, Q. T. Zhang, and L. Zhang, *Ceram. Int.*, 42, 13855 (2016).
25. M. Rajendran, S. K. Samal, and S. Vaidyanathan, *Journal of Alloys & Compounds*, 815, 152631 (2020).
26. X. F. Zhou, W. Y. Geng, J. Y. Ding, Y. C. Wang, and Y. H. Wang, *Dyes Pigm.*, 152, 75 (2018).
27. J. Y. Yu, Y. F. Fan, L. N. Wu, B. Sun, and Y. L. Wu, *ECS J. Solid State Sci. Technol.*, 10, 056004 (2021).
28. L. Ozawa, *J. Electrochem. Soc.*, 126, 106 (1979).
29. A. I. Becerro, M. Allix, M. Laguna, D. González-Mancebo, C. Genevois, A. Caballero, G. Lozano, N. O. Núñez, and M. Ocaña, *J. Mater. Chem. C*, 12830 (2018).
30. S. Bai, Y. Liu, G. Tan, W. Liu, D. Liu, R. Wang, Y. Zhu, S. Ye, and H. Ren, *J. Lumin.*, 117351 (2020).
31. H. Cheng et al., *Journal of Alloys & Compounds*, 161343 (2021).
32. L. Guerbous, M. Derbal, and J. P. Chaminade, *J. Lumin.*, 130, 2469 (2010).
33. F. Xie, D. Xu, Z. Wu, M. S. Mohokeev, B. Milcevic, H. Li, and J. Shi, *J. Lumin.*, 227, 117516 (2020).
34. X. Mi, J. Sun, P. Zhou, H. Zhou, D. Song, K. Li, M. Shang, and J. Lin, *J. Mater. Chem. C*, 3, 4471 (2015).
35. J. Zhou and Z. Xia, *Opt. Mater.*, 53, 116 (2016).
36. J. L. Wu, Z. Zhang, J. Chen, S. Chen, J. Cao, and H. Guo, *J. Lumin.*, 232, 117857 (2021).
37. R. Yantake, A. Sidike, and T. Yusuufu, *J. Rare Earths*, 40, 390 (2022).
38. G. Blasse, *Phys. Lett.*, 28A, 444 (1968).
39. D. L. Dexter and J. H. Schulman, *J. Chem. Phys.*, 22, 1063 (1954).
40. R. Reisfeld and N. Lieblich-Soffer, *J. Solid State Chem.*, 28, 391 (1979).
41. L. Han, X. Z. Xie, J. H. Lian, Y. H. Wang, and C. W. Wang, *J. Lumin.*, 176, 71 (2016).
42. X. Min, M. H. Fang, Z. H. Huang, Y. G. Liu, C. Tang, and X. W. Wu, *J. Am. Ceram. Soc.*, 98, 788 (2015).
43. L. Zhao, D. D. Meng, Y. Y. Li, Y. Zhang, and H. Q. Wang, *Journal of Alloys & Compounds*, 728, 564 (2017).
44. X. C. Yu, Y. L. Jiang, X. J. Li, Y. Song, X. Zhang, H. N. Liu, B. Y. Zhao, T. Ye, L. Duan, and J. B. Fan, *Crystengcomm*, 24, 805 (2022).
45. Z. Q. Zheng, P. Z. Xie, P. P. Yi, J. Zhao, L. H. Liu, and F. C. Yi, *J. Lumin.*, 221, 117052 (2020).