Abstract: A series of Dy$^{3+}$ ion doped Sr$_2$CaWO$_6$ phosphors with double perovskite structure were synthesized by traditional high temperature solid-state method. It was found that there is significant energy transfer between Dy$^{3+}$ and the host lattice, and the intensities of emission peaks at 449 nm (blue), 499 nm (cyan), 599 nm (orange), 670 nm (red), and 766 nm (infra-red) can be changed by adjusting the concentration of dopant amount of Dy$^{3+}$ ion in Sr$_2$CaWO$_6$. The correlated color temperature of Dy$^{3+}$ ion doped Sr$_2$CaWO$_6$ phosphors can be tuned by adjusting the concentration of Dy$^{3+}$ ion. Upon optimal doping at 1.00 mol% Dy$^{3+}$, white light with chromaticity coordinate (0.34, 0.33) was emitted under excitation at 310 nm. Thus, single composition white emission is realized in Dy$^{3+}$ doped Sr$_2$CaWO$_6$.

Keywords: photoluminescence; white light-emitting; double perovskite; energy transfer

1. Introduction

In recent years, phosphor-covered white light-emitting diodes (pc-WLEDs) have become more and more prevalent due to their superior performance, such as energy saving, long life time, small volume, and high brightness, compared to the conventional white light sources [1]. The commercial approach for obtaining white light-emitting diode (WLED) typically involves covering blue chips with yellow light-emitting phosphors such as Y$_3$Al$_5$O$_{12}$:Ce$^{3+}$ (YAG:Ce$^{3+}$). Nevertheless, the lack of strong visible red-light emission makes it difficult to fabricate WLEDs with a high color-rendering index (CRI) and low correlated color temperature (CCT) [2–6], which limit their applications. In order to overcome these difficulties, red, green, and blue (RGB) tricolor phosphors pumped by ultra-violet (UV) LED chips (300–400 nm) are used to fabricate WLEDs with high CRI. However, it is difficult to fabricate WLED with high conversion efficiency as there is strong reabsorption of the blue-light by the green and red phosphors [7,8]. Thus, single-composition white light-emitting phosphors pumped by near ultra-violet (n-UV) light-emitting diodes are desired to fabricate WLEDs [9–11].

Double perovskite has the formula of A$_2$BB’O$_6$ [12,13]. The tungstate with double perovskite structure has important physical properties, such as magnetic [14], electrical [15], photocatalytic [16], and optical properties [17]. The luminescence properties of [WO$_6$]$^{6-}$ group in A$_2$BWO$_6$ has been reported [18]. As previously reported, the emission colors of [WO$_6$]$^{6-}$ group in A$_2$BWO$_6$ could range from blue to yellow (e.g., Ba$_2$CaWO$_6$, blue; Sr$_3$WO$_6$, green, and Ba$_3$MgWO$_6$, yellow), which strongly depends on the choice of A and B ions [18]. Rare earth (RE) ion doped double perovskite tungstate
has been shown to have promising photoluminescence properties [19], such as Ba₂CaWO₆:Eu³⁺ [20], Ba₂ZnWO₆:Eu³⁺, Li⁺ [17], Sr₂CaWO₆:Eu³⁺, Na⁺ [21], and Sr₂CaWO₆:Sm³⁺, Na⁺ [22]. The emission peak at yellow region of Dy³⁺ ion which corresponding to the transition of 4F₉/₂ → 6H₁₃/₂ is greatly influenced by the coordination environment [23]. Furthermore, the ratio of emission peak intensities in blue (4F₉/₂ → 6H₁₃/₂) and yellow (4F₉/₂ → 6H₁₃/₂) region for Dy³⁺ ion is influenced by the coordination environment, and when there is an inversion center the emission in blue region is of significant intensity [24].

In the present work, Dy³⁺ was used to replace the Ca²⁺ ion in Sr₂CaWO₆, which is with an inversion center. Single-composition white light emitting phosphors with tunable correlated color temperature were successfully synthesized by adjusting the concentration of Dy³⁺ ions. There are some single-composition white light emission phosphors materials can be obtained at near ultra-violet(n-UV), such as Ca₉Gd(PO₄)₇:Eu²⁺, Mn²⁺ [25], NaBaBO₃:Dy³⁺, K⁺ [26], and Sr₃Y(PO₄)₃:Dy³⁺ [27]. However, many materials need UV excitation under 300 nm to realize white light emission, such as Y(PO₄)₃:Dy³⁺ [28], β-GdB₃O₆:Bi³⁺, Tb³⁺, Eu³⁺ [29], LaNbO₄:Dy³⁺ [30], and LuNbO₄:Dy³⁺ [31]. Taking LuNbO₄:Dy³⁺ as example, the excitation peak of LuNbO₄:Dy³⁺ phosphors centered in 261 nm. In comparison, Sr₂CaWO₆:Dy³⁺ phosphors can be excited under a relatively longer wavelength of 310 nm. In the present work, the photoluminescence properties of Dy³⁺ ions doped Sr₂CaWO₆ with different concentrations of Dy³⁺ ions and white light emission upon optimal doping are reported.

2. Material and Methods

The powder samples of Sr₂Ca(1−1.5x%)WO₆: x mol% Dy³⁺ (x = 0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0) and Sr₂Ca₀.₉₉WO₆: 0.5 mol% Dy³⁺, 0.5 mol% M⁺ (M⁺ = Li⁺, Na⁺, K⁺) were synthesized by high-temperature solid-state method. The starting materials SrCO₃ (99.9%, Sigma-Aldrich), CaCO₃ (99.95–100.05%, Alfa), WO₃ (99.90%, Adamas), Li₂CO₃ (99%, Alfa), Na₂CO₃ (99.8%, General-Reagent), K₂CO₃ (99%, Sigma-Aldrich), and Dy₂O₃ (99.9%, Adamas) were weighed by stoichiometric ratio. Then the starting materials were mixed and ground in an agate mortar. The mixture was transferred to a corundum crucible and preheated under 850 °C for 5 h in a box furnace. After the sample was cooled down to room temperature, the mixture was thoroughly ground, calcined at 1200 °C for 12 h, cooled to room temperature, and reground to obtain the final powder sample.

The powder XRD date of Sr₂Ca(1−1.5x%)WO₆: x mol% Dy³⁺ (x = 0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0) were collected in the range of 10° ≤ 2θ ≤ 70° using a Rigaku D/MAX 2550 diffract meter (Cu-Kα, λ = 1.54059 Å), operated at 40 kV and 40 mA. The UV–Vis absorption spectra of Sr₂CaWO₆ and Sr₂CaWO₆: doped with 1 mol% Dy³⁺ were collected with a UV–Vis spectrometer (Lambda 950, Perkin-Elmer, Waltham, MA, USA) with a polytetrafluoroethylene plate as a reference. The excitation spectra and emission spectra were collected with a photoluminescence spectrometer (FS5, Edinburgh Instruments, Livingston, UK) equipped with a 150 W xenon lamp as the excitation source. The lifetime of Sr₂Ca₀.₉₉WO₆: 1.00 mol% Dy³⁺ was measured with an FLS-980 fluorometer (Edinburgh Instruments, Livingston, UK).

3. Results and Discussion

3.1. Structural characterization

XRD patterns were collected to determine the phases of Sr₂Ca(1−1.5x%)WO₆: x mol% Dy³⁺ (x = 0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0). Meanwhile, we also characterized the structure of Sr₂Ca₀.₉₉WO₆: 0.5% Dy³⁺, 0.5 mol% M⁺ (M⁺ = Li⁺, Na⁺, K⁺), for which Li⁺, Na⁺, and K⁺ ions were introduced as charge compensators. The ionic radius of Dy³⁺ ion in six-fold coordination is 0.912 Å, close to Ca²⁺ ion, which has an ionic radius of 1.0 Å for six-fold coordination, while the ionic radius of Sr²⁺ ion is 1.44 Å [32]. As shown in Figure 1a, the XRD patterns of Sr₂Ca(1−1.5x%)WO₆: x mol% Dy³⁺ (x = 0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0) matched well with JPCDS card of Sr₂CaWO₆ (JPCDS #76-1983). As shown in Figure 1b, compared with JPCDS cards of Sr₂CaWO₆, the XRD patterns of Sr₂Ca₀.₉₉WO₆: 0.5 mol% Dy³⁺, 0.5 mol% M⁺ (M⁺ = Li⁺, Na⁺, or K⁺) have no obvious change. Thus, the introduction of the
charge compensator has little influence on the crystal structure of Sr$_2$CaWO$_6$. These results indicated that the host structure of double perovskite was well preserved for both the samples with and without charge compensators.

The host compound Sr$_2$CaWO$_6$ is in orthorhombic system with $Pmm2$ space group ($a = 8.1918$ Å, $b = 5.7653$ Å, $c = 5.8491$ Å, $V = 276.24$ Å$^3$). In the host lattice of Sr$_2$CaWO$_6$, with the formula of $A_2BB'O_6$, Ca$^{2+}$ ions and W$^{6+}$ ions reside at B and B’ sites, respectively. Ca atoms and W atoms are coordinated by 6 O atoms (Figure 2). The cations and the coordinated oxygen ions form an octahedral structure with an inversion center. Each CaO$_6$ octahedron shared its O atoms with six adjacent WO$_6$ octahedron, and each WO$_6$ octahedron also shared its O atoms with six adjacent CaO$_6$ octahedron. Sr atoms are located at the interspace of CaO$_6$ octahedron and WO$_6$ octahedron and coordinated by 12 O atoms, without an inversion center [21,22].

**Figure 1.** (a). The X-ray diffraction patterns of Sr$_2$Ca$_{(1-1.5x\%)}$WO$_6$: x mol% Dy$^{3+}$ (x = 0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0); (b). The X-ray diffraction patterns of Sr$_2$CaWO$_6$, Sr$_2$Ca$_{0.9925}$WO$_6$: 0.5 mol% Dy$^{3+}$ and Sr$_2$Ca$_{0.99}$WO$_6$: 0.5 mol% Dy$^{3+}$, 0.5 mol% M$^+$(M$^+ = $ Li$^+$, Na$^+$, or K$^+$).
Figure 2. The crystal structure of Sr$_2$CaWO$_6$ in which Sr atoms are marked with green ball, gray WO$_6$ octahedrons and cerulean CaO$_6$ octahedron are shown to represent coordination of W atoms and Ca atoms.

3.2. UV–Vis Absorption Spectra

The UV–Vis absorption spectrum of Sr$_2$CaWO$_6$ is shown in Figure 3a. There is a broad absorption band in UV region. The calculated band structure and partial densities of Sr$_2$CaWO$_6$ and the atoms constituting Sr$_2$CaWO$_6$, such as strontium, calcium, tungsten, and oxygen have been reported before [22]. The strong absorption in the ultraviolet region 270–330 nm is attributed to the charge transfer from O atom to W atom. With the UV–Vis absorption spectra, the optical band gap ($E_g$) of Sr$_2$CaWO$_6$ can be calculated with the following equation [33]:

\[ \alpha h \nu = k (h \nu - E_g)^n \]

where $\alpha$ is the absorbance, $h$ is the Planck’s constant, $\nu$ is the frequency, $k$ is a constant, $n$ is equal to 1/2, 2, 3/2, or 3, which is dependent on whether the transition is direct allowed, indirect allowed, direct forbidden of indirect forbidden, respectively. Wang et al reported the calculated band structure of Sr$_2$CaWO$_6$ and the result indicated that the Sr$_2$CaWO$_6$ is an indirect band gap insulator [22]. Considering the transition is indirect allowed, here $n = 2$. The optical band gap of Sr$_2$CaWO$_6$ is calculated to be 3.79 eV, while the optical band gap of Sr$_2$CaWO$_6$: 1.0 mol% Dy$^{3+}$ is 3.81 eV (Figure 3b). The optical band gap of Sr$_2$CaWO$_6$ synthesized by sol-gel method was calculated to be 3.51 eV, which is 0.30 eV smaller than the value obtained from the present sample [22]. This suggests that the preparation conditions have appreciable influence on the optical band gap.
3.3. Luminescence Properties

The photoluminescence excitation spectra of Sr$_2$CaWO$_6$ (1−1.5x%) WO$_6$: x mol% Dy$^{3+}$ (x = 0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0), which were measured at emission wavelength of 499 nm, are shown in Figure 4a. As shown in Figure 4a, there is a broad excitation band in the region of 270–330 nm. The calculated band structure and total densities of states of Sr$_2$CaWO$_6$ near the Fermi energy level have been reported [22]. The broad excitation band centered at 310 nm was attributed to the charge transfer from O$^{2−}$ to W$^{6+}$ ions. The doping concentrations of Dy$^{3+}$ ion have significant influence on the excitation band of the host lattice. With the increase of doping concentration, the excitation intensity at 310 nm decreased. The concentration dependent excitation intensity of phosphors at 310 nm is shown in Figure 4b.
with introducing charge compensation ions, which indicated that the defects caused by the introduction of charge compensation ions cause more energy loss. The emission spectra of Sr$_2$Ca$_{0.99}$WO$_6$:0.5 mol% Dy$^{3+}$, 0.5 mol% M$^+$ (M$^+$ = Li$^+$, Na$^+$ or K$^+$). The introduction of charge compensation ions had no significant influence on the emission of Dy$^{3+}$ ion doped Sr$_2$CaWO$_6$ phosphors. A broad emission band centered at 449 nm, which is due to self-trapped luminescent recombination in [WO$_6$]$_{6-}$ octahedral [19,34]. The emission peaks at 499 nm ($^4F_{9/2} \rightarrow ^6H_{15/2}$), 599 nm ($^4F_{9/2} \rightarrow ^6H_{13/2}$), 670 nm ($^4F_{9/2} \rightarrow ^6H_{11/2}$) and 766 nm ($^4F_{9/2} \rightarrow ^6H_{9/2}$) are attributed to f-f transitions of Dy$^{3+}$ ions. As shown in Figure 5a, the emission intensity of Sr$2$Ca$_{0.99}$WO$_6$: 0.5 mol% Dy$^{3+}$, 0.5 mol% M$^+$ decreased in different degrees with introducing charge compensation ions, which indicated that the defects caused by the introduction of charge compensation ions cause more energy loss. The emission spectra of Sr$_2$Ca$_{1−x}$(1−x)WO$_6$: x mol% Dy$^{3+}$ (x = 0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0) is shown in Figure 5b. The concentration-dependent emission intensity variations at 449 nm, 499 nm, 599 nm and 670 nm are shown in Figure 5c.

The photoluminescence emission spectra of Dy$^{3+}$ doped Sr$_2$CaWO$_6$ phosphors were collected under excitation at 310 nm. Figure 5a shows the emission spectra of Sr$_2$Ca$_{0.99}$WO$_6$: 0.5 mol% Dy$^{3+}$, 0.5 mol% M$^+$ (M$^+$ = Li$^+$, Na$^+$ or K$^+$). The introduction of charge compensation ions had no significant influence on the emission of Dy$^{3+}$ ion doped Sr$_2$CaWO$_6$ phosphors. A broad emission band centered at 449 nm, which is due to self-trapped luminescent recombination in [WO$_6$]$_{6-}$ octahedral [19,34]. The emission peaks at 499 nm ($^4F_{9/2} \rightarrow ^6H_{15/2}$), 599 nm ($^4F_{9/2} \rightarrow ^6H_{13/2}$), 670 nm ($^4F_{9/2} \rightarrow ^6H_{11/2}$) and 766 nm ($^4F_{9/2} \rightarrow ^6H_{9/2}$) are attributed to f-f transitions of Dy$^{3+}$ ions. As shown in Figure 5a, the emission intensity of Sr$_2$Ca$_{0.99}$WO$_6$: 0.5 mol% Dy$^{3+}$, 0.5 mol% M$^+$ decreased in different degrees with introducing charge compensation ions, which indicated that the defects caused by the introduction of charge compensation ions cause more energy loss. The emission spectra of Sr$_2$Ca$_{1−x}$(1−x)WO$_6$: x mol% Dy$^{3+}$ (x = 0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0) is shown in Figure 5b. The concentration-dependent emission intensity variations at 449 nm, 499 nm, 599 nm and 670 nm are shown in Figure 5c.

The electric dipole transition of $^4F_{9/2} \rightarrow ^6H_{13/2}$ emission of Dy$^{3+}$ ion is sensitive to surrounding environment [24]. If there is no inversion center, the $^4F_{9/2} \rightarrow ^6H_{13/2}$ emission of Dy$^{3+}$ ions will be strong. Otherwise, the $^4F_{9/2} \rightarrow ^6H_{13/2}$ emission of Dy$^{3+}$ ion will be weak. However, the transition of $^4F_{9/2} \rightarrow ^6H_{15/2}$ is not as sensitive to coordinate surroundings [24,35]. Therefore, the symmetry of the environment in which Dy$^{3+}$ ions are located can be judged by comparing the relative intensity...
of $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ and $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ transition [36]. In most fluorescent materials, with Dy$^{3+}$ ions in the asymmetric position the transition intensity of $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ is much stronger than that of $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ (such as SrMoO$_4$:Dy$^{3+}$ [37], LuNbO$_4$:Dy$^{3+}$ [31], and Sr$_2$ZnWO$_6$:Dy$^{3+}$ [19]). With Dy$^{3+}$ ion located at a position with high symmetry, the transition intensity of $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ is almost the same as that of $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$, or even weaker than that of $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ (such as Ba$_3$La$_2$$_{-x}$(BO$_3$)$_4$:xDy$^{3+}$ [38], Ba$_2$Ca$_{(1-x)}$WO$_6$:xDy$^{3+}$ [20], Sr$_3$Sc$_{1-x}$(PO$_4$)$_3$:xDy$^{3+}$ [39]). As can be seen from the emission spectra of Dy$^{3+}$ ion doped Sr$_2$CaWO$_6$, the emission intensity of $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{15/2}$ at 499 nm is similar to $^4\text{F}_{9/2} \rightarrow ^6\text{H}_{13/2}$ centered at 599 nm, which indicates that Dy$^{3+}$ replaces the position with high symmetry.
phosphors with tunable correlated color temperature were successfully generated through adjusting the concentration of Dy. 499 nm, 599 nm, and 670 nm changed with concentration of Dy. Deereased with the increase of the concentration of Dy. 3+ ions. The excitation spectra of Dy 3+ ions have significant overlap with the emission spectra of Sr2CaWO6, and there is energy radiation transfer from Sr2CaWO6 to the f-f transition absorptions of Dy 3+ ions. Hence, the emission peak intensity at 449 nm decreased with the increase of the concentration of Dy 3+ ion, while the emission peak intensities at 499 nm, 599 nm, and 670 nm changed with concentration of Dy 3+ ion when x > 1.0. However, when x > 1.0, the emission peak intensities at 499 nm, 599 nm, 670 nm, and 766 nm increased with higher doping concentration of Dy 3+ ion when x > 1.0. The concentration-dependent emission intensity variations at 449 nm, 499 nm, 599 nm and 670 nm respectively.

As shown in Figure 6, the excitation peaks located at 352 nm, 366 nm, and 455 nm are attributed to the f-f transition absorptions of Dy 3+ ions. The excitation spectra of Dy 3+ ions have significant overlap with the emission spectra of Sr2CaWO6, and there is energy radiation transfer from Sr2CaWO6 host lattice (donors) to Dy 3+ ions (acceptors) [40]. Hence, the emission peak intensity at 449 nm decreased with the increase of the concentration of Dy 3+ ion, while the emission peak intensities at 499 nm, 599 nm, 670 nm, and 766 nm increased with higher doping concentration of Dy 3+ ion when x ≤ 1.0. However, when x > 1.0, the emission peak intensities at 499 nm, 599 nm, 670 nm, and 766 nm decreased with the increase of the concentration of Dy 3+ ion. The emission peak-intensities at 449 nm, 499 nm, 599 nm, and 670 nm changed with concentration of Dy 3+ ion, and single-composition WLED phosphors with tunable correlated color temperature were successfully generated through adjusting the concentration of Dy 3+ ion.

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Figure 5. (a) Emission spectrum of Sr2Ca0.99WO6: 0.5 mol% Dy3+, 0.5 mol% M+ (M+ = Li+, Na+ or K+) under 310 nm excitation; (b) Emission spectrum of Sr2Ca(1−1.5%x)%WO6: x mol% Dy3+ (x = 0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0) under 310 nm excitation. (c) The concentration-dependent emission intensity variations at 449 nm, 499 nm, 599 nm and 670 nm respectively.

Figure 6. The excitation spectrum of Sr2Ca0.985WO6: 1 mol% Dy3+ (λem = 499 nm) is shown in black, and the emission spectrum of Sr2CaWO6 under 310 nm excitation is shown in red.
The critical distance \((R_c)\) between Dy\(^{3+}\) ions were calculated by the concentration quenching method. The critical transfer distance \((R_c)\) was calculated with the following formula (Equation (2)) which was proposed by Blasse [41]:

\[
R_c \approx 2 \left[ \frac{3V}{4\pi x_c N} \right]^{\frac{1}{3}} \tag{2}
\]

In this equation, \(V\) is the volume of crystallographic unit cell, \(x_c\) is the critical concentration, and \(N\) is the lattice site number in a unit cell which can be replaced by sensitizers. In \(\text{Sr}_2\text{CaWO}_6\), \(V = 276.24\ \text{Å}^3, N = 2, \text{and } x_c = 0.01, R_c \) of Dy\(^{3+}\) ion is calculated to be 29.8 Å. In general, for the energy transfer process, the exchange interaction and multipole interaction are the two mechanisms that can play important roles [40]. Exchange interactions take place over a distance shorter than 5 Å, while multipole interaction can occur at a distance as large as 30 Å [42,43]. The critical distance of Dy\(^{3+}\) ion in \(\text{Sr}_2\text{CaWO}_6\) equal to 29.8 Å, which is much larger than 5 Å. Therefore, the energy transfer process belongs to multipole interaction instead of exchange interaction.

Van Uitert [40] has pointed out that when non-radiative losses are attributed to multipolar transfer, the strength of multipolar interaction can be determined from the change in the emission intensity of activator. The relation between the emission intensity of each activator and the concentration of each activator can be expressed by Equation (3) [44,45]:

\[
\lg I_x = -\frac{s}{3} \lg x + A \tag{3}
\]

where \(I\) is the integral emission intensity of \(^6F_{5/2} \rightarrow ^4H_{13/2}\), \(x\) is the corresponding doping concentration, \(A\) is a constant which independent on the dopant concentration, and \(s\) is dependent on the interaction process. The value of \(s\) can be 6, 8, and 10, corresponding to electric dipole–dipole, electric dipole–quadrupole or electric quadrupole–quadrupole interaction, respectively. When \(s\) equal to 3, the energy transfer among nearest-neighbor ions plays a major role in quenching. As shown in Figure 7, the slope was calculated to be \(-0.87\), thus \(s\) is most approximate 3. Therefore, the energy transfer process is most likely caused by energy transfer among nearest-neighbor ions.

![Figure 7](image)

**Figure 7.** The function relation between \(\lg (I/x)\) and \(\lg x\).

Figure 8 shows the decay curve of \(\text{Sr}_2\text{CaWO}_6\): 1.00 mol% Dy\(^{3+}\) phosphors excited at 310 nm and monitored at 499 nm. The decay curve fits well with the following single-exponential Equation (4):

\[
I(t) = A \exp \left( -t/\tau \right) \tag{4}
\]
where $I(t)$ is the emission intensity at time $t$ and $A$ is a constant. Thus, the lifetime value of $\tau$ is calculated to be 0.48 ns. The reported lifetime value of $\text{Sr}_{1.99}\text{CaWO}_6:0.01\text{Dy}^{3+}$ is 127 $\mu$s [34]. Therefore, synthesis methods and doping sites appear to have significant influence on fluorescence lifetime.

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**Figure 8.** Decay curve of $\text{Sr}_2\text{CaWO}_6:1.00 \text{ mol\% Dy}^{3+}$ at room temperature with $\lambda_{ex} = 310$ nm and $\lambda_{em} = 499$ nm.

The proposed energy transfer mechanism of $\text{Sr}_2\text{CaWO}_6:\text{Dy}^{3+}$ phosphors are shown in Figure 9. In $\text{Sr}_2\text{CaWO}_6$, electrons at valence band top were excited under 310 nm ultraviolet irradiation and transferred to conduction band, which is mainly attributed to the charge transfer from O atoms to W atoms. Electrons at conduction band returned to conduction band bottom through non-radiative transition. When electrons at conduction band bottom transfer to the top of valance band, energy is released by radiative transition. Thus, there is a broad blue light emission band in $\text{Sr}_2\text{CaWO}_6$. In $\text{Sr}_2\text{Ca}(1-1.5x\%)\text{WO}_6: x \text{ mol\% Dy}^{3+}$ phosphors, besides the excitation of charge transfer from O atoms to W atoms, $\text{Dy}^{3+}$ ions are also excited by the ultraviolet under 310 nm. $\text{Dy}^{3+}$ ions can be excited to energy levels higher than $4F_{9/2}$ by visible light from 350 nm until 450 nm. Electrons at high energy levels return to $4F_{9/2}$ configuration through non-radiative transition, then release to $6H_{J}$ ($J = 11/2$, $13/2$, $15/2$) configuration through radiative transition. It is well known that $\text{Dy}^{3+}$ ions have matched energy level pairs which produce strong cross relaxation and lead to concentration quenching. Therefore, it can be inferred that besides the energy transfer among nearest-neighbor ion, the concentration quenching is also related to cross relaxation of $\text{Dy}^{3+}$ ions ($4F_{9/2}:6H_{15/2} \rightarrow 6H_{9/2} + 6F_{11/2}:6F_{3/2}$ and $4F_{9/2}:6H_{15/2} \rightarrow 6F_{5/2}:6H_{7/2} + 6F_{9/2}$, where $6H_{9/2} + 6F_{11/2}$ and $6H_{7/2} + 6F_{9/2}$ mean the energy level of $6H_{9/2}$ and $6H_{7/2}$ are very close to those of $6F_{11/2}$ and $6F_{9/2}$, respectively) [45].
As the doping concentration continues to increase, the CIE coordinates gradually shift to the yellow region (0.37, 0.36). By adjusting the concentration of Dy$^{3+}$ ion, a series of phosphors with different CIE coordinates were successfully obtained and white light from a single host was successfully obtained (Figure 10).

3.4. Commission International de l’Eclairage (CIE) chromaticity diagram

As shown in Table 1, with the increase of doping concentration, the CIE coordinates of Sr$_2$Ca$_{(1-1.5x\%)}$WO$_6$: $x$ mol% Dy$^{3+}$ phosphors can be adjusted from the blue region (0.18, 0.16) to white (0.34, 0.33) ($x = 1$), which is very close to the coordinate of standard white light (0.33, 0.33). As the doping concentration continues to increase, the CIE coordinates gradually shift to the yellow region (0.37, 0.36). By adjusting the concentration of Dy$^{3+}$ ion, a series of phosphors with different CIE coordinates were successfully obtained and white light from a single host was successfully obtained (Figure 10).

Table 1. Commission International de l’Eclairage (CIE) coordinates of different Dy$^{3+}$ ion concentration of Sr$_2$CaWO$_6$.

| Number | Phosphors | CIE Coordinates (x,y) |
|--------|-----------|-----------------------|
| 1      | Sr$_2$CaWO$_6$ | (0.18, 0.16) |
| 2      | Sr$_2$Ca$_{0.9985}$WO$_6$:0.001Dy$^{3+}$ | (0.23, 0.21) |
| 3      | Sr$_2$Ca$_{0.9955}$WO$_6$:0.003Dy$^{3+}$ | (0.27, 0.26) |
| 4      | Sr$_2$Ca$_{0.9925}$WO$_6$:0.005Dy$^{3+}$ | (0.30, 0.29) |
| 5      | Sr$_2$Ca$_{0.99}$WO$_6$:0.005Ddy$^{3+}$:0.005Li$^+$ | (0.30, 0.29) |
| 6      | Sr$_2$Ca$_{0.99}$WO$_6$:0.005Dy$^{3+}$:0.005Na$^+$ | (0.29, 0.28) |
| 7      | Sr$_2$Ca$_{0.99}$WO$_6$:0.005Dy$^{3+}$:0.005K$^+$ | (0.29, 0.28) |
| 8      | Sr$_2$Ca$_{0.985}$WO$_6$:0.010Dy$^{3+}$ | (0.34, 0.33) |
| 9      | Sr$_2$Ca$_{0.9775}$WO$_6$:0.015Dy$^{3+}$ | (0.35, 0.34) |
| 10     | Sr$_2$Ca$_{0.97}$WO$_6$:0.020Dy$^{3+}$ | (0.37, 0.36) |
| 11     | Sr$_2$Ca$_{0.955}$WO$_6$:0.030Dy$^{3+}$ | (0.37, 0.36) |
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Author Contributions:
Data curation, Y.D. and S.Y.; Formal analysis, Y.D.; Investigation, Y.D.; Methodology, Y.D., Y.S., C.-G.D., H.P., F.Y. and Q.Z.; Resources, Y.D.; Writing—original draft, Y.D.; Writing—review & editing, Fan Yang and Qingbiao Zhao.

References

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4. Conclusions

In summary, phosphors with Dy$^{3+}$ doped on the Ca site of Sr$_2$CaWO$_6$ were prepared by high temperature solid state method, and they can be excited under 310 nm ultraviolet. The host compound, Sr$_2$CaWO$_6$ emits blue light centered at 449 nm with the color coordinate of (0.18, 0.16) under ultraviolet excitation at 310 nm. The intensity of emission peaks under 310 nm excitation can be tuned by adjusting the concentration of Dy$^{3+}$ ion. White light emission with CIE coordinate (0.34, 0.30) and Sr$_2$Ca$_{0.99}$WO$_6$:0.5 mol% Dy$^{3+}$, 0.5 mol% M$^+$ (M$^+$ = Li$^+$, Na$^+$ or K$^+$) were compared at various Dy$^{3+}$ ion concentration. It can be seen that the CIE coordinates of the samples with and without charge compensation ions are very close (Figure 10). Therefore, the introduction of charge compensation ion does not significantly affect the chromaticity coordinates.

Figure 10. CIE 1931 color coordinates of Sr$_2$Ca$_{(1-1.5x%)}$WO$_6$: x mol% Dy$^{3+}$ (x = 0, 0.1, 0.3, 0.5, 1.0, 1.5, 2.0, 3.0) and Sr$_2$Ca$_{0.99}$WO$_6$: 0.5 mol% Dy$^{3+}$, 0.5 mol% M$^+$ (M$^+$ = Li$^+$, Na$^+$ or K$^+$).

Chromaticity coordinates of Sr$_2$Ca$_{(1-1.5x%)}$WO$_6$: x mol% Dy$^{3+}$ (x = 0, 0.1, 0.3, 0.5, 1.0, 2.0, 3.0) and Sr$_2$Ca$_{0.99}$WO$_6$: 0.5 mol% Dy$^{3+}$, 0.5 mol% M$^+$ (M$^+$ = Li$^+$, Na$^+$ or K$^+$) were compared at various Dy$^{3+}$ ions.

In summary, phosphors with Dy$^{3+}$ doped on the Ca site of Sr$_2$CaWO$_6$ were prepared by high temperature solid state method, and they can be excited under 310 nm ultraviolet. The host compound, Sr$_2$CaWO$_6$ emits blue light centered at 449 nm with the color coordinate of (0.18, 0.16) under ultraviolet excitation at 310 nm. The intensity of emission peaks under 310 nm excitation can be tuned by adjusting the concentration of Dy$^{3+}$ ion. White light emission with CIE coordinate (0.34, 0.33) was successfully generated in Sr$_2$CaWO$_6$:Dy$^{3+}$ phosphors at the doping level of 1 mol% on the Ca site. Considering the overlap between the emission spectra of host lattice and the excitation spectra of Dy$^{3+}$ ions, it is expected that there is efficient energy transfer from host lattice to Dy$^{3+}$ ions.

Author Contributions: Data curation, Y.D. and S.Y.; Formal analysis, Y.D.; Investigation, Y.D.; Methodology, Y.D., Y.S., C.-G.D., H.P., F.Y. and Q.Z.; Resources, Y.D.; Writing—original draft, Y.D.; Writing—review & editing, F.Y. and Q.Z.

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