

Article

Effect of Rb⁺ Doping on Tunable Luminescence in Yb³⁺/Er³⁺-Y₂O₃ Film

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Received: 27 October 2020; Accepted: 19 November 2020; Published: 23 November 2020



Abstract: In this paper, a series of Rb⁺-doped Er³⁺/Yb³⁺-Y₂O₃ films were synthesized via a sol-gel method and spin coating. The structure and morphology of the samples were investigated by X-ray diffraction and scanning electron microscopy. The Rb⁺-doped films with nanoparticles, in the size range of 20–40 nm, were obtained. The spectroscopic analysis of the samples was investigated by using the emission spectra and the intensity of luminescence. All the samples exhibited a green emission ascribed to ²H_{11/2}/⁴S_{3/2} to ⁴I_{15/2} of Er³⁺ and a red one ascribed to ⁴F_{9/2} and its stark level to ⁴I_{15/2} of Er³⁺. As the Rb⁺ concentration increased, the intensities of the green light and red light were enhanced 16.97- and 5.81-fold relative to that of the undoped sample. Moreover, by controlling the Rb⁺ concentration, the samples were capable of generating color-tunable luminescence from red to green linearly. The tunable emission was caused by the change of ion distribution ratio in ⁴F_{7/2}(Er) and ⁴F_{9/2}(Er) levels. The results suggest that the as-prepared Rb⁺-doped Er³⁺/Yb³⁺-Y₂O₃ films have a great potential for applications of luminescence.

Keywords: Rb⁺ doping; color adjustment; rare earth luminescence; Y₂O₃; sol-gel

1. Introduction

In recent years, rare earth (RE) ion-doped upconversion (UC) luminescent materials, which can gather energy via the process of absorbing two or more long-wavelength low-energy photons and then emitting a short-wavelength high-energy photon, have attracted much more attention [1–3]. Because of this property, RE-doped luminescent materials are widely used in many areas, such as display [4], solar cells [5], biological fluorescence imaging [6], phosphors [7], UC lasers [8], and optical communications [9].

Since RE-doped luminescent materials were proposed, luminescence improvements have always been the focus of research [10]. Scholars have proposed many ways to enhance luminescence [11–13]. First, the proper doping ratio of the activator and sensitizer can enhance luminescence. Second, according to the J–O theory [14], reducing the symmetry of the lattice can enhance emissions. Third, changing the surface structure of the material and reducing the defect can reduce energy loss and enhance emission. In practical applications, these methods are often combined to enhance luminescence [15,16].

Theoretically, the host lattice symmetry and the distance between rare earth ions can be changed when the doping ion substitutes the matrix cation. According to the Dexter theory [17], energy transfer

efficiency is inversely proportional to the distance between rare earth ions in a certain range. Therefore, elements with a larger ion radius, which can better regulate the distance between rare earth ions, are good choices for enhancing luminescent efficiency. At present, a lot of research studies on doping with a larger ion radius, such as Na and K, have been investigated. The Na⁺-doped Ca₃(PO₄)₂: Tb³⁺ exhibits a comparable brightness with commercial Zn₂SiO₄: Mn²⁺ [18]. For K⁺-doped core-shell luminescent nanoparticles, the detection sensitivity can be improved obviously [19]. For Li⁺, Na⁺, and K⁺-codoped Dy³⁺: B₂O₃–Al₂O₃–ZnO–Bi₂O₃–BaO–M₂O (M = Li, Na, and K) multicomponent barium bismuth borate glasses, each alkali metal ion has a different function in the modulation of white light [20]. In order to further improve the luminescence properties of RE luminescent materials, optimal doping elements, concentrations, and mechanisms still need to be further studied.

In our previous works, the effects of alkali metals such as Na⁺ and Li⁺ in Yb³⁺/Er³⁺ co-doped Y₂O₃ films were studied. It was found that a change of energy accumulation in upconversion luminescence and the light switching effect in the ultraviolet region can be observed by using Li⁺ doping and Na⁺ doping, and the effect of the inhibition of light emission was studied. In the present work, Rb⁺-Yb³⁺/Er³⁺ codoped Y₂O₃ films were prepared via a sol-gel and spin coating technique, and the effects of Rb⁺ doping on the structure and luminescence properties of the films were investigated. Moreover, the mechanisms of emission were discussed with the aim of understanding emission behaviors.

2. Experimental Details

2.1. Preparation

A Y₂O₃–Rb (with Yb³⁺ and Er³⁺) precursor was prepared using a sol-gel method. All chemicals were used directly without further purification. The preparation process is shown in Figure 1.

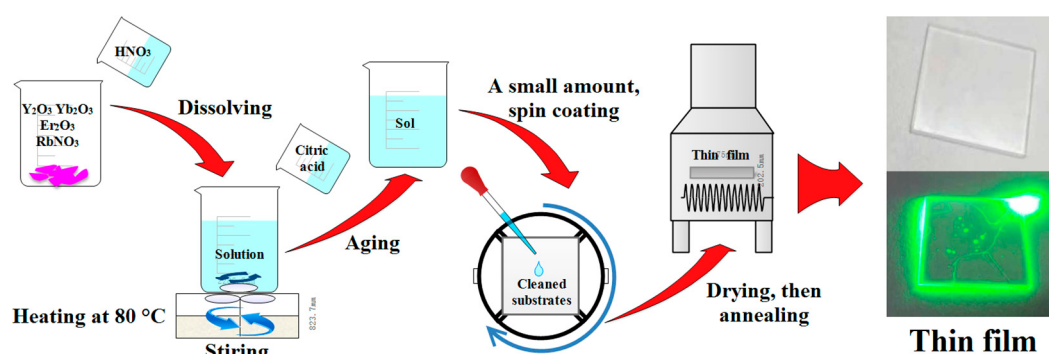


Figure 1. The preparation process for the films.

Substrate preparation: Quartz glass was chosen as the substrate. It was cleaned with deionized water first, then cleaned with ethanol by ultrasonic bath for 30 min. Next, it was cleaned with dilute sulfuric acid solution for 30 min, and then cleaned with dilute alkali solution by ultrasonic bath for 2 h, and finally, by deionized water again.

Sol preparation: Y₂O₃ (3N, 99.9%), Yb₂O₃ (3N, 99.9%), Er₂O₃ (3N, 99.9%), and RbNO₃ (3N, 99.9%) were mixed according to the ions' ratio in Table 1 and dissolved at a certain concentration of nitric acid. Then citric acid was added into the solution, and the solution was then stirred at 80 °C for half of 1 h. Thus the precursor sol was ready.

Film deposition: the precursor sol was aged at room temperature for 24 h. And then the sol was deposited onto the glass substrate with spin coating to form gel films. The films were dried in air at 200 °C for 30 min, followed by an annealing process at 1000 °C for 2 h. Films with a thickness of about 500 nm, which is an appropriate thickness to balance luminescence performance, transmittance, and mechanical strength, were obtained.

Table 1. The relative mole ratios of all kinds of ions.

Sample Name	Y ³⁺	Er ³⁺	Yb ³⁺	RE ³⁺ (Er ³⁺ + Yb ³⁺): Rb ⁺
Rb-1	100	2	5	1:0
Rb-2	100	2	5	1:1
Rb-3	100	2	5	1:1.5
Rb-4	100	2	5	1:2
Rb-5	100	2	5	1:2.5
Rb-6	100	2	5	1:3

2.2. Characterization

The film's morphology was observed with a field-emission scanning electron microscope (FE-SEM, Hitachi S4800, Hitachi, Tokyo, Japan). The crystal structure of each film was characterized with X-ray diffraction (XRD, Bruker, Billerica, MA, USA, BRUKER D8 DISCOVER, 0.154056 nm wavelength, 0.02° step length, 10° to 90° diffraction angle). The films' Fourier-transform infrared spectroscopy (FTIR) spectra were measured with a Nicolet iS50 instrument (Thermo Scientific, Tokyo, Japan). The photoluminescence spectrum was obtained with a Hitachi F-4500 instrument (Hitachi, Tokyo, Japan). The wavelength of the pump laser was 980 nm. The luminescence decay was measured with a fluorescence spectrometer (FLS 1000, Edinburgh Instruments, Livingston, UK). The chromaticity coordinate (CIE) and brightness of the samples were recorded using a CS-100A luminance meter (Konica Minolta, Tokyo, Japan), with a light beam area of about 1 mm². All analytical tests were done at room temperature.

3. Results and Discussion

3.1. Phase Components and Structure

The surface morphologies of the samples were characterized by SEM. All the samples had almost the same surface morphology, and only sample Rb-5 is given as a representative in Figure 2. Meanwhile, the chemical composition analysis of sample Rb-5 with an EDS spectrogram is given in the inset in Figure 2. The surface of the film is compact, crystallized well, and composed of round nanoparticles. As shown in the inset in Figure 2, the Y³⁺ characteristic peak at 2.0 keV is the highest, and other elements' characteristic peaks are also clearly shown in the spectrum, which means that the main phase should be Y₂O₃, and Rb⁺-doped Er³⁺/Yb³⁺-Y₂O₃ films can be obtained.

The structure of the films was characterized by XRD. The samples' diffraction peaks were clear and sharp, indicating that all the samples had high crystallinity, as shown in Figure 3 for sample Rb-5. According to the standard cards of Y₂O₃ (PDF#41-1105), all the main diffraction peaks could be indexed to the characteristic peaks of (211), (222), (400), (440), and (622) lattice planes of the cubic phase structure of Y₂O₃. The XRD patterns of all the samples were very similar, and the location of their characteristic peaks was basically the same, which indicates that neither the RE³⁺ ions nor the Rb⁺ ion doping changed the basic structure of the lattice and the Rb⁺ ion should have been incorporated into the lattice of matrix Y₂O₃.

In order to further explore the effect of Rb⁺ ions on the matrix lattice, the diffraction peaks of the main crystal plane (222) were amplified, as shown in the inset in Figure 3. It is obvious that with the Rb⁺ concentration increase, the (222) peak shifts to a low angle, which should be attributed to small radius ions Y³⁺ (0.89 Å) replaced by large radius ions Rb⁺ (1.48 Å). According to Bragg's law, $2d\sin\theta = n\lambda$, where d is the interplanar crystal spacing, θ is the angle between the incident X-ray and crystal face, n is the series of the diffraction, and λ is the X-ray wavelength (0.154056 nm). When large radius ions replace small radius ions, the main diffraction peak shifts to a low angle, and the lattice constant is also changed. According to the Debye–Scherrer formula [21], $D = k\lambda/(\beta\cos\theta)$, where D is the average grain size of the nanocrystals, λ is the X-ray wavelength (0.154056 nm), θ is the Bragg angle of the diffraction peak, k is the Scherrer constant that is conventionally set to 0.89, and β is the

corrected full width at half maximum (FWHM) of the main diffraction characteristic peak of the XRD pattern. The average size of the grains for each film is calculated, and the results are listed in Table 2. Nanocrystal sizes in the range of 20–40 nm can be obtained after Rb^+ ion doping.

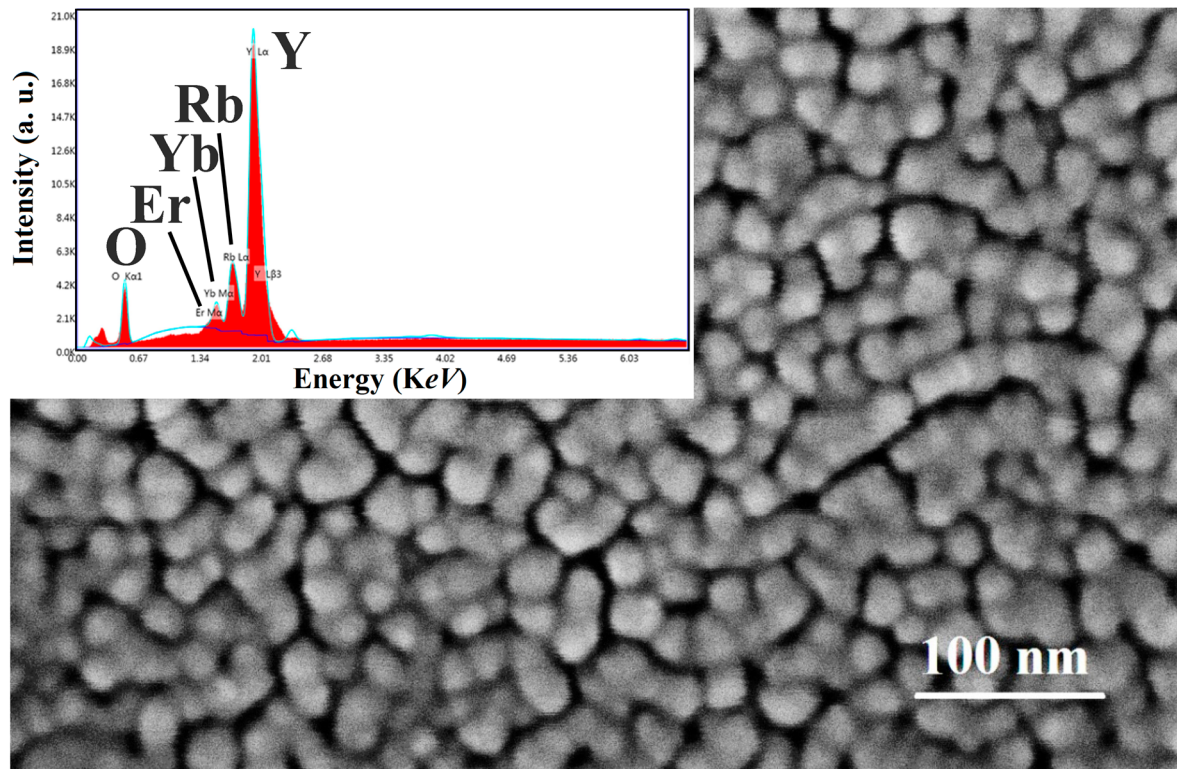


Figure 2. The surface morphology of sample Rb-5. The inset is an EDS spectrogram of Rb-5.

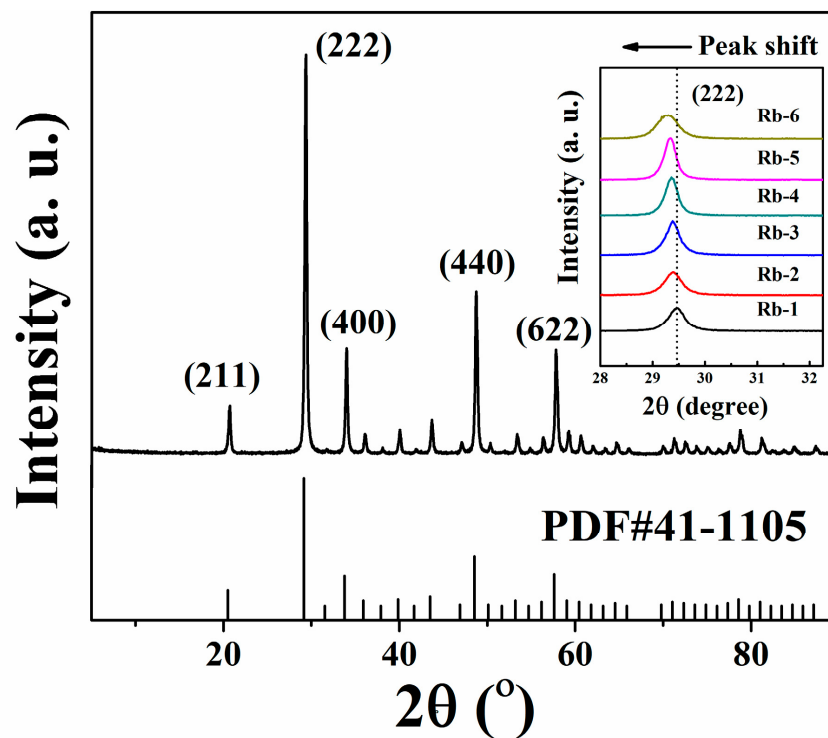
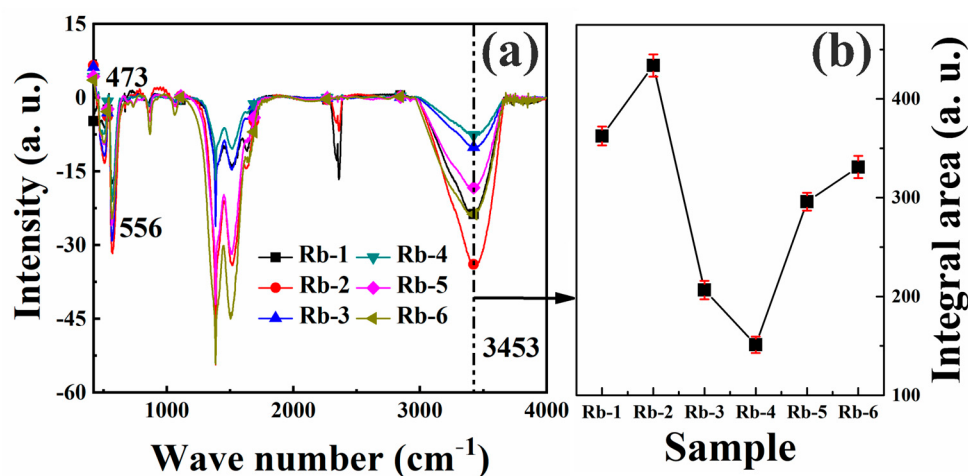


Figure 3. XRD patterns of sample Rb-5. The inset is the shift of the main diffraction peaks (222) of the samples.

Table 2. Main peak position (222), average lattice, and average grain sizes of the samples.

Sample	Peak Position (222)	Crystal Constant (Å)	Average Grain Sizes (nm)
Rb-1	29.461°	10.511	24.1
Rb-2	29.403°	10.532	38.0
Rb-3	29.379°	10.533	29.5
Rb-4	29.361°	10.543	36.6
Rb-5	29.337°	10.550	19.0
Rb-6	29.263°	10.568	23.0

Figure 4a shows the FTIR spectra of the samples. Each curve has strong sharp characteristic absorption peaks at 473, 566, and 3453 cm^{-1} corresponding to the asymmetric stretching vibrations of the Y–O bond and the RE–O bond, the symmetric stretching vibrations of the Y–O–Y bond and the RE–O–RE bond, and the peak of the –OH respectively. All the curves are highly similar, and the positions of the main absorption peaks are almost the same, which indicates that Rb^+ ion doping has no great influence on the main structure of the lattice. In order to observe the wide absorption peak of the –OH bond, coming from water absorbed due to surface defects of the samples [22], the spectrum integral in the range of 2700–3900 cm^{-1} was calculated and is shown in Figure 4b. Surface defect is the absorption center of energy, which is not conducive to the energy transfer of luminescence. The value of the integral area of sample Rb-1 is strong, and when Rb^+ doping concentration increases, the value increases for Rb-2, then decreases, and at last increases again, which indicates that surface defects of the films can be reduced by Rb^+ doping.

**Figure 4.** (a) FTIR spectra of the samples; (b) the curve of the normalized peak strength area integral of the samples.

3.2. PL Luminescence

In order to understand the effect of Rb^+ on the probability of the nonradiative transition between rare earth ions, the luminescence decay curves of the samples were tested. The curves of the green emission are shown in Figure 5, which are similar to those of the red emission. According to the fitting formula [23], $R(t) = A + B_1\exp(-t/\tau_1) + B_2\exp(-t/\tau_2)$, where $R(t)$ is the intensity of the luminescence; τ_1 and τ_2 are decay times; A , B_1 , and B_2 are constants; and t_1 and t_2 are decay times, the average decay times of the samples were calculated, as shown in Table 3. It can be seen that the decay times for the Rb^+ -doped samples are longer than that for the undoped sample, and the extreme value points were obtained for sample Rb-3. According to the Dexter theory [24,25], the energy transfer efficiency is inversely proportional to the distance between sensitized and activated ions. As a result, the increase of fluorescence decay time should be caused by the decrease of the distance between Yb^{3+} and Er^{3+} . Additionally, the decrease of fluorescence decay time, further increasing Rb^+ doping concentration, should be caused by fluorescence quenching.

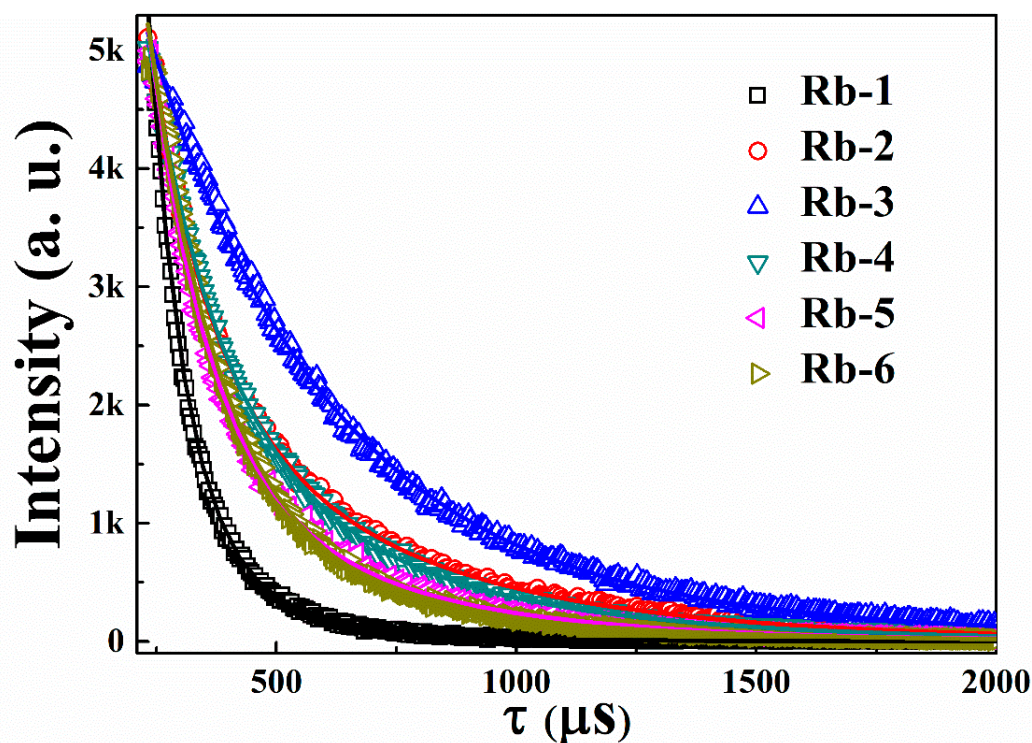


Figure 5. Luminescence decay curves of green emission for films.

Table 3. Decay times obtained from an exponential fit of the room temperature decay curves for 556 nm green emission and 660 nm red emission.

Sample	Green Emission ($\lambda_{em} = 556$ nm)			Red Emission ($\lambda_{em} = 660$ nm)		
	τ (μ s) (Rel %)	τ (μ s) (Rel %)	Avg. Decay Time μ s	τ (μ s) (Rel %)	τ (μ s) (Rel %)	Avg. Decay Time μ s
Rb-1	60.65 (68.85%)	141.20 (31.15%)	86.45	74.36 (63.72%)	215.22 (36.28%)	130.02
Rb-2	117.99 (29.64%)	388.41 (70.36%)	318.23	158.74 (37.73%)	550.48 (62.27%)	413.22
Rb-3	165.33 (36.85%)	411.40 (63.15%)	340.95	333.70 (62.81%)	790.78 (37.19%)	514.71
Rb-4	126.42 (40.28%)	350.29 (59.72%)	275.33	172.56 (46.08%)	511.33 (53.92%)	365.96
Rb-5	91.44 (41.65%)	293.31 (58.35%)	221.31	135.89 (48.66%)	445.21 (51.34%)	302.84
Rb-6	82.65 (46.03%)	257.01 (53.97%)	181.84	146.71 (58.73%)	426.44 (41.27%)	217.18

Figure 6a illustrates the luminescence spectra of the samples in the range of 450–750 nm excited with a 980 nm pump laser at a constant power of 1 W. All the spectra exhibited both green emission (520–570 nm) ascribed to $^2H_{11/2}/^4S_{3/2}$ to $^4I_{15/2}$ of Er^{3+} and red emission (640–680 nm) ascribed to $^4F_{9/2}$ and its stark level to $^4I_{15/2}$ of Er^{3+} . The emission intensities of all the samples were much stronger in the red region than in the green region. Moreover, the positions of the strongest peak moved from 660 to 659 nm, which indicates that Rb^{+} slightly altered the magnitude of the splitting of Er in the Y_2O_3 crystal field, leading to the $^4F_{9/2}(Er)$ level having a slight down shift. For small UC version rates, the luminescence intensity, I_{UC} , follows the relation $I_{UC} \propto P_{pump}^n$, where P_{pump} is the incident pump power and n is the number of photons required to populate the emitting state. The plot of I_{UC} versus P_{pump} with a double logarithmic scale yields a straight line with a slope n . Figure 6c shows the logarithmic plot of sample Rb-3. The values of n are 2.016 and 1.785 for the green and red emissions, which indicates that the green and red emissions are both two-photon processes [26]. The peak area integrals of the green and red emissions are shown in Figure 6b. For both emissions, with the increase of Rb^{+} doping concentration, the peak intensity first increases, then decreases, and finally increases. The emission intensity values of green and red of sample Rb-3 were improved 16.97 and 5.81 times compared with those of the original ones, respectively.

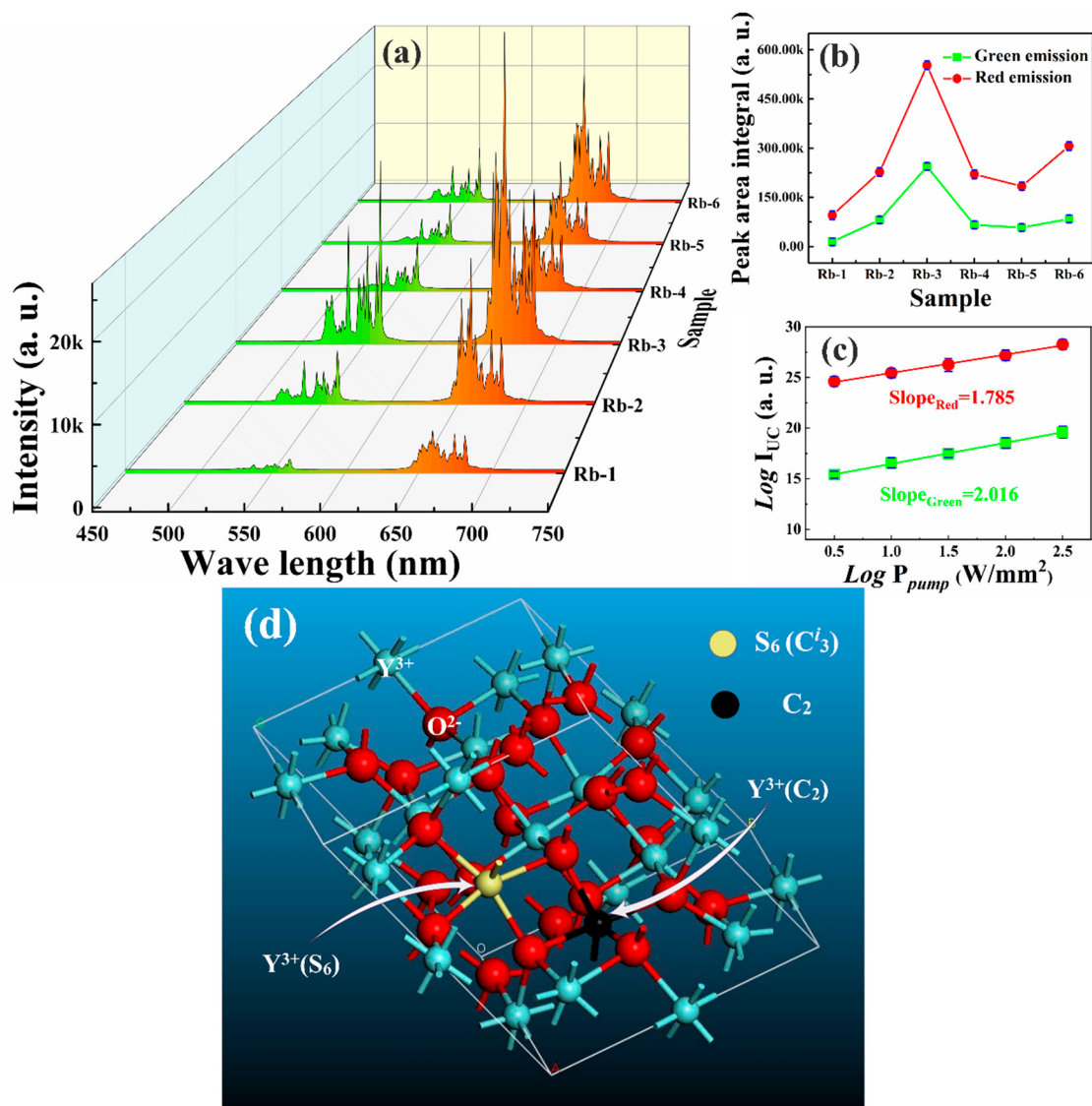


Figure 6. (a) Effect of Rb^+ on the photoluminescence (PL) spectra; (b) the main peaks' area integral of the spectra; (c) dependence of luminescence intensity on pump power (Rb-3); (d) Y_2O_3 lattice diagram.

For further investigation of the luminescence of the films, the lattice structure of doped Y_2O_3 can be described according to the standard card of Y_2O_3 (PDF#41-1105). As shown in Figure 6d, Er^{3+} , Yb^{3+} , and Rb^+ in the films replace the Y^{3+} ions and are located in both high-symmetry S_6 lattice points and asymmetric C_2 lattice points. According to the rare earth luminescence theory, energy level transitions only occur in rare earth ions that are located in asymmetric positions. When Rb^+ is doped, the lattice can be enlarged, and the original symmetry is broken. As a result, the high-symmetry S_6 points change into asymmetric points. RE ions at these points would be activated and participate in the luminescence. Meanwhile, the enlarged lattice caused by Rb^+ doping would squeeze the neighboring lattices, which can make RE ions closer. As the concentration of Rb^+ doping increases, the distance between RE ions is reduced, and the luminous efficiency should be greatly improved. According to the discussion above, the increase of both emissions of films should be caused by the increase of active RE ions and the decrease of distance between RE ions. As Rb^+ doping concentration is further increased, the sharp reduction of luminescence intensity should be caused by concentration quenching. The final slight enhancement of emission can be attributed to the increase of an effective luminescence center, which is caused by the increase of crystal size as shown in Table 2.

The Commission Internationale de l'Eclairage (CIE) chromaticity diagram of the films are shown in Figure 7c, and an enlarged view is given in Figure 7b. It can be seen that the coordinates of the Rb⁺-doped samples jump to the green region from the red region compared with the undoped sample, which indicates that the energy density of the Rb⁺-doped film is higher than that of the undoped sample. Moreover, it is observed that the color coordinate points are approximately aligned on a line, which indicates that the luminescence of the samples after Rb⁺ doping keeps the color uniformity, and the light emission of the samples is mainly adjusted by the green light and red light.

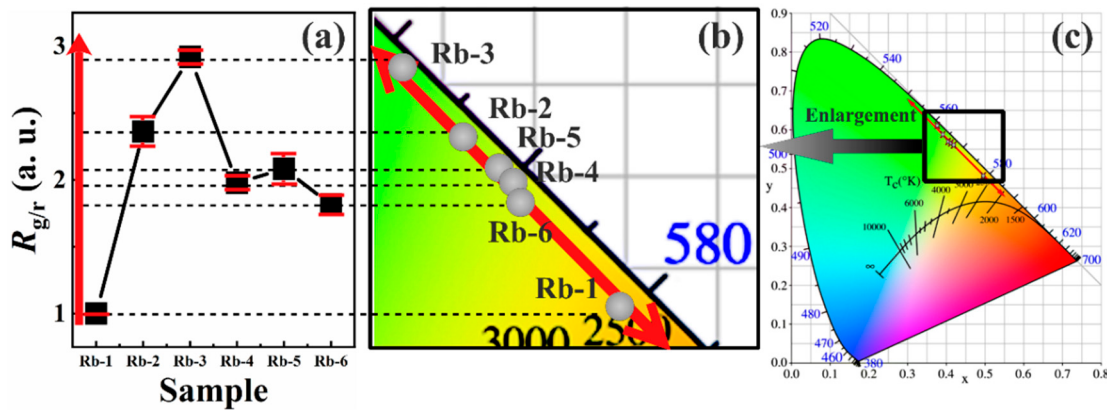


Figure 7. (a) The ratios of the emission enhancement multiple; (b) zoom of the Commission Internationale de l'Eclairage (CIE) chromaticity diagram; (c) the CIE chromaticity diagram.

It is known that the ratios of the emission enhancement multiple are related to color coordinates [27]. In order to further explore the regularity of color coordinate change, the ratios of the green emission enhancement multiple to the red emission ($R_{g/r}$) are calculated and shown in Figure 7a according to the following equation:

$$R_{g/r}(\text{Rb} - x) = \frac{E_{\text{Rb}-x}(\text{Green})}{E_{\text{Rb}-1}(\text{Green})} / \frac{E_{\text{Rb}-x}(\text{Red})}{E_{\text{Rb}-1}(\text{Red})} \quad (1)$$

where E is the emission peaks' area integral and Rb- x represents Rb-1, Rb-2, Rb-3, Rb-4, Rb-5, and Rb-6. It can be seen that the value of $R_{g/r}$ increases and then decreases with the increase of Rb⁺ doping concentration, which indicates that the distribution of excited ions for the green emission and red emission is changed with Rb⁺ doping. According to Figure 7a,b, the color coordinates change from the red region to the green region as $R_{g/r}$ increases, which allows us to linearly adjust the color coordinates by adjusting the Rb⁺ doping concentration.

3.3. The Mechanisms of Energy Transfer and Emissions

The energy-level diagram of the Er³⁺-Yb³⁺ ion pair is depicted in Figure 8a. The green emission process can be indexed in two ways. First, $^2F_{7/2}(\text{Yb}) + 980 \text{ nm laser} \rightarrow ^2F_{5/2}(\text{Yb})(\text{GSA})$, $^2F_{5/2}(\text{Yb}) \rightarrow ^4I_{11/2}(\text{Er})(\text{ET1, where ET is Energy transfer})$; $^4I_{11/2}(\text{Er}) + ^2F_{5/2}(\text{Yb}) \rightarrow ^4F_{7/2}(\text{Er})(\text{ESA, ET2})$, $^4F_{7/2}(\text{Er})$ undergoes nonradiative decay to $^2H_{11/2} \rightarrow ^4I_{15/2}$ (535 nm green emission); $^4F_{7/2}(\text{Er})$ undergoes nonradiative decay to $^4S_{3/2} \rightarrow ^4I_{15/2}$ (556 nm green emission). Second, $^4I_{15/2}(\text{Er}) + 980 \text{ nm laser} \rightarrow ^4I_{11/2}(\text{Er})(\text{GSA})$, $^4I_{11/2}(\text{Er}) + ^4F_{7/2}(\text{Er}) \rightarrow ^2H_{11/2}(^4S_{3/2})(\text{Er}) + ^4F_{9/2}(\text{Er})(\text{CR})$, $^2H_{11/2}(^4S_{3/2}) \rightarrow ^4I_{15/2}$ (535 and 556 nm green emission), where GSA is ground state absorption, ESA is excited state absorption, ET is energy transfer, and CR is cross relaxation.

The red emission process can be indexed in three ways. First, $^4F_{7/2}(\text{Er})$ undergoes nonradiative decay to a slightly lower level, $^4F_{9/2} \rightarrow ^4I_{15/2}$ (660 nm red emission). Second, $^4I_{11/2}(\text{Er})$ releases energy to the matrix $\rightarrow ^4I_{13/2}$, $^4I_{13/2}(\text{Er}) + ^2F_{5/2}(\text{Yb}) \rightarrow ^4F_{9/2}(\text{Er})(\text{ET3})$, $^4F_{9/2}$ and its stark level $\rightarrow ^4I_{15/2}$ (660 or 673 nm red emission). Third, $^4I_{11/2}(\text{Er}) + ^4F_{7/2}(\text{Er}) \rightarrow ^2H_{11/2}(^4S_{3/2})(\text{Er}) + ^4F_{9/2}$ and its stark level (Er)(CR), $^4F_{9/2}$ and its stark level of $^4F_{9/2} \rightarrow ^4I_{15/2}$ (660 or 673 nm red emission).

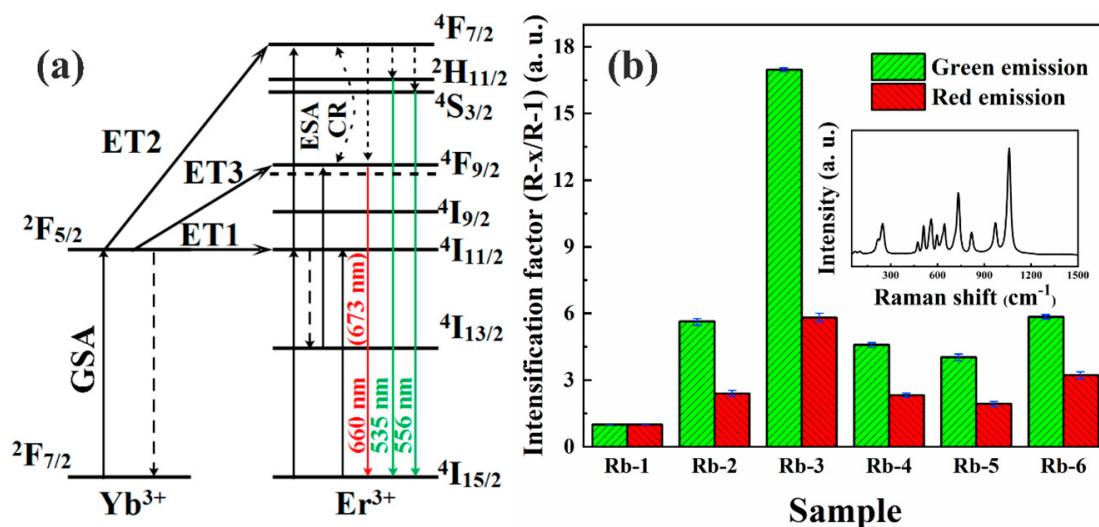


Figure 8. (a) Energy level diagram and the mechanisms; (b) enhancement of luminescence. The inset is Raman spectra.

As can be seen in Figure 8b, the emission intensifications of green and red are different, which indicates that the distribution of excited ions in energy levels changes. According to the energy level transition mechanism, generally, there are two factors that cause the change of excited ion distribution, phonon energy and the distance between rare earth ions. The Raman spectra of the samples were tested, which shows a similar profile as shown in the inset in Figure 8b, indicating that Rb^+ doping has no effect on the phonon energy of the samples [28]. Therefore, the distance change between rare earth ions is the main reason for the linear change of color coordinates. As discussed in fluorescence lifetimes, the energy transfer efficiency can be increased by decreasing the distance between Yb^{3+} and Er^{3+} caused by Rb^+ doping, which indicates that the distribution of excited ions in energy levels can be changed by Rb^+ doping. As shown in Figure 8a, the green emission comes from the $4F_{7/2}(\text{Er})$ level, and the red emission comes from the $4F_{7/2}(\text{Er})$ and ET3 process. When color coordinates move to the green region from the red region by increasing the Rb^+ doping concentration, the green emission gets more enhancement amplitude, which indicates that there are more excited ions located in $4F_{7/2}(\text{Er})$ compared with $4F_{9/2}$ levels. By using Rb^+ -doped films, energy transfer efficiency between Yb^{3+} and Er^{3+} can be improved, and the preferential distribution of excited ions in the $4F_{7/2}(\text{Er})$ level is obtained.

4. Conclusions

A series of $\text{Rb}^+-\text{Er}^{3+}/\text{Yb}^{3+}$ -codoped Y_2O_3 luminescence films with various concentrations of Rb^+ ions were prepared via a sol-gel method and spin coating. The doped films with nanoparticles were obtained, and the Rb^+ ions' effect on the luminescence was investigated. Rb^+ doping can reduce the surface defects and increase the fluorescence lifetime of the film. The intensity of the green and red emissions for the doped samples can be enhanced 16.97 and 5.81 times compared with that of the original ones, respectively. The ratio of the green emission enhancement amplitude to the red emission enhancement amplitude was calculated, which is related to the position of the color coordinates. The results show that the excited ions' distribution can be changed in energy levels by Rb^+ doping, which leads to the $2F_{5/2}(\text{Yb}) \rightarrow 4I_{11/2}(\text{Er})$ and $4I_{11/2}(\text{Er}) + 2F_{5/2}(\text{Yb}) \rightarrow 4F_{7/2}(\text{Er})$ process and the $4I_{13/2}(\text{Er}) + 2F_{5/2}(\text{Yb}) \rightarrow 4F_{9/2}(\text{Er})$ process being tunable. As a result, the emission with linearly adjusted color can be obtained.

Author Contributions: Conceptualization, B.X., C.S., and J.L.; Methodology, B.X.; Software, B.X.; Validation, C.S., J.S. (Jun Song), R.H., and J.L.; Formal Analysis, B.X. and C.S.; Investigation, B.X.; Resources, B.X., Z.L., Y.Z., J.S. (Jie Song), and H.L.; Data Curation, B.X. and C.S.; Writing—Original Draft Preparation, B.X.; Writing—Review & Editing, B.X.; Visualization, B.X.; Supervision, B.X., C.S., and J.L.; Project Administration, C.S., J.S. (Jun Song), R.H., and J.L.; Funding Acquisition, C.S., J.S. (Jun Song), R.H., and H.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Natural Science Foundation of China (nos. 61, 274, 140, and 61306003); Natural Science Foundation of Guangdong Province (2015A030313871); Young Talents in Higher Education of Guangdong, China 2017 (2017KQNCX129); and Science and Technology Planning Projects of Chaozhou (2018GY18).

Conflicts of Interest: The authors declare no conflict of interest.

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