Rare Metal Materials and Engineering
Volume 46, Issue 6, June 2017
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: Rare Metal Materials and Engineering, 2017, 46(6): 1524-1529.

ARTICLE

Effect of Li Content, Deposition Time and Solution Concentration on Morphology and Photoluminescence Properties of Y_2O_3: 5%Eu^{3+}, *x*%Li^+ Thin Film

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Abstract: Y_2O_3: 5%Eu^{3+}, *x*%Li^+ phosphor thin film was fabricated via an electro-deposited method. The dependence of the morphology and luminescent properties for Y_2O_3: 5%Eu^{3+}, *x*%Li^+ thin film on Li content, deposition time and solution concentration were studied. The results indicate that the morphology and the emission intensity strongly depend on the Li content, deposition time, and solution concentration. It is found that the Li addition is beneficial to the formation of flower morphology and then enhances the photoluminescence intensity. The optimal Li content is 15% for Y_2O_3: 5%Eu^{3+}, *x*%Li^+.

Key words: phosphor thin film; electro-deposited method; Li-doped

Y_2O_3 has been investigated due to its superior properties and widely used in white light emitting diodes, plasma display panels, and cathode ray tubes [1-3]. It is well known that Li^+ ions as the dopants play an important role in increasing the luminescent efficiency of bulk and nano-sized phosphors. Wang[4] etc. found that the luminescent intensity could be greatly enhanced by doping Li^+ ions in Y_2O_3:Ho^{3+}/Yb^{3+} and Er^{3+}/Li^+ co-doped Sb_2O_3-Na_2O-SiO_2 glasses. The phosphors intensity of Tm^{3+} ions of Y_2O_3:Tm^{3+}/Yb^{3+} can be enhanced by about 14 times with 5mol% Li^+ ions[5]. The reasons for the emission intensity enhancement by doping Li^+ ions are attributed to the modification of the local symmetry around the Er^{3+}/Yb^{3+}/Ho^{3+} ion, the reduction of OH^- groups, and the creation of the oxygen vacancies in the phosphors.

Now, various techniques have been developed for Y_2O_3:Eu^{3+} nano-size compound synthesis over the past decades, typically including combustion [6], sol-gel[7], and thermal plasma processing[8]. The phosphor films have also been prepared using electron-beam evaporation [9], pulsed laser deposition (PLD) [10], sol-gel techniques[11], and electro-deposition[12].

Here, the electro-deposition method was adopted to prepare Y_2O_3: 5%Eu^{3+}, *x*%Li^+ thin film and then morphology and luminescent properties were also probed.

1 Experiment

All samples were prepared by electro-deposition in a conventional three-electrode cell. The working electrode was FTO (fluorine doped tin oxide film) coated glass, counter electrode was a platinum foil, and the reference electrode was Ag/AgCl/saturated KCl. The initial materials were $Y(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$, and $LiNO_3$. Firstly, different amounts of the starting materials $Y(NO_3)_3 \cdot 6H_2O$, $Eu(NO_3)_3 \cdot 6H_2O$ and $LiNO_3$ were dissolved in deionized water under stirring and heating until the uniform and transparent solution were formed. The molar concentration of the solution was 0.1 mol/L. Secondly, the

Received date: May 18, 2016
Foundation item: National Natural Science Foundation of China (11204001, 11174004); Anhui Provincial Natural Science Foundation (1308085MA04); Higher Educational Natural Science Foundation of Anhui Province (KJ2013A031); Anhui University Scientific Research Fund (201410357005, KYXL2013009)
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above solution was ready for electro-deposition. The applied potential was –1.2 V versus Ag/AgCl/saturated KCl for each sample. The deposition temperature was 60 ℃ for each sample. The deposition time was 0.5, 1.0, and 1.5 h, separately. After deposition, the samples were annealed in air at 600 ℃. The crystal structures of these samples were characterized by X-ray diffraction using an X-ray diffractometer (XRD, DX-2000 SSC) with Cu Kα radiation (λ=0.15418 nm) over a scanning range of 10°~70° with a step of 0.02°. Scanning electron microscopy (SEM, S-4800, Hitachi) and high resolution transmission electron microscopy (TEM, JEOL JEM-2100) were used to observe the morphologies and microstructures. FTIR spectra of the phosphor powders were recorded on a Nicolet IR-200 spectrometer with KBr pellet technique from 4000 to 400 cm^{-1}. The excitation and emission spectra were measured on a FL fluorescence spectrophotometer (F-4500,Hitachi). The luminescence lifetime was collected by one EasyLife fluorescence spectrometer. All the measurements were carried out at room temperature.

2 Results and Discussion

2.1 Effect of Li content on the structure morphology and luminescent properties of Y_2O_3: 5% Eu^{3+}, x% Li^+

Fig.1 shows XRD patterns of the Y_2O_3: 5%Eu^{3+}(L00), Y_2O_3:5%Eu^{3+}, 12%Li^+ (L12), and Y_2O_3:5%Eu^{3+},21%Li^+ (L21). The XRD patterns are matched with JCPDS (No.89-5592) patterns of Y_2O_3, which has a cubic structure with space group Ia(206). The XRD patterns exhibit standard peaks at 2θ of 20.50°, 29.08°, 33.74°, 48.40°, and 57.50° assigned to (211), (222), (400), (440), and (622) planes, respectively. The results show the Y_2O_3 lattice is not disturbed by the insertion of Eu^{3+} and Li^+ ions.

The thickness and structure of the films are presented in Fig.2. The thickness is about 30~50 μm. Fig.2c is the low magnification SEM image for Y_2O_3:5%Eu^{3+}, 12% Li^+. It can be observed that the sample is composed of a large number of uniform flower-like nano-structures, whose average diameter is about 4 μm. The close inspection of the high-magnification image reveals that these flowers are made up of many thin petals with a smooth and large surface, and that the thickness is about 0.5~1.0 μm (shown as Fig.2d). Fig.2e shows that the TEM image for Y_2O_3:5%Eu^{3+}, 12%Li^+ has conspicuous hierarchical structures like flowers, which is consistent with the SEM images. A single petal peeled from Y_2O_3:5%Eu^{3+}, 12%Li^+ micro-flower was investigated carefully as shown in Fig.2f. It is clearly found that the petal is composed of a plenty of nano-particles with diameter about 50 nm even smaller via the weak self-assembly. In other words, the petals used to con-structure Y_2O_3:Eu^{3+}(5%), Li^+(x%) micro-flowers is the

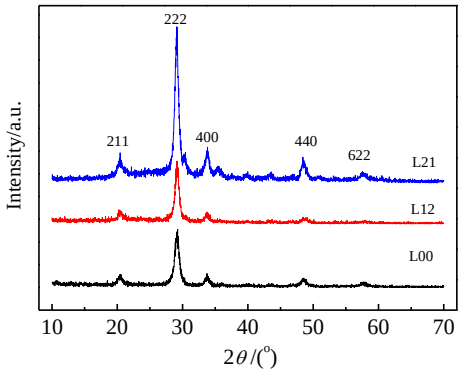

Fig.1 XRD patterns of Y_2O_3:5%Eu^{3+}(L00), Y_2O_3:5%Eu^{3+}, 12%Li^{3+} (L12), and Y_2O_3:5%Eu^{3+}, 21%Li^{3+} (L21)

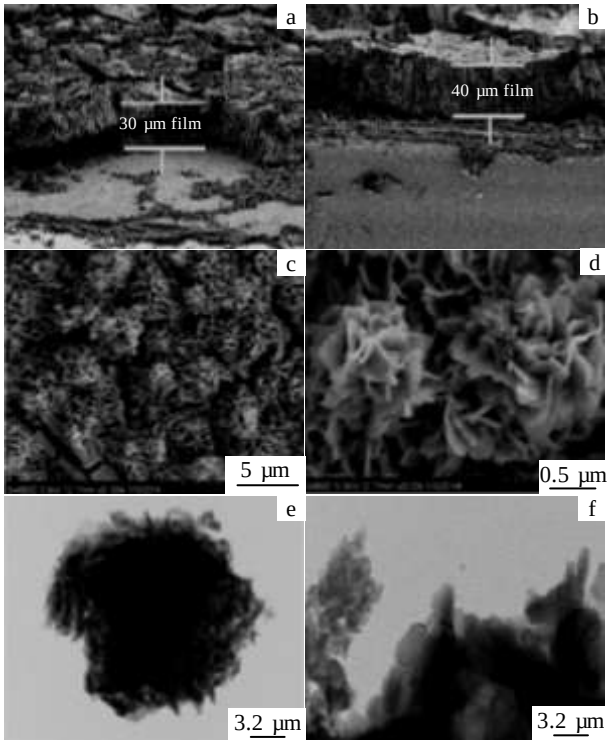

Fig.2 TEM images of cross-section for Y_2O_3:5%Eu^{3+}, 12%Li^+ (a, b); SEM images for Y_2O_3:5%Eu^{3+}, 12%Li^+ with low amplification (c) and with high amplification (d); TEM images for a whole flower (e) and for one petal (f)

collections of nano-particles weakly bond together (as shown in Fig.2f).

To investigate the growth process of the self-assembled flower-like micro-architectures, six different solutions: Y_2O_3: 5%Eu^{3+}; Y_2O_3:5%Eu^{3+}, 3%Li^+; Y_2O_3:5%Eu^{3+}, 6%Li^+; Y_2O_3: 5%Eu^{3+}, 12% Li^+; Y_2O_3:5%Eu^{3+}, 21%Li^+; Y_2O_3:5% Eu^{3+}, 24%Li^+ were prepared with other synthetic conditions remaining unchanged. The morphologies are observed and

shown in Fig.3. Without Li doping, there are many flakes attached with each other and no-flower shapes are observed, as presented in Fig.3a. While with adding 3%Li dopants into the sample, it is clearly seen that these flakes begin to aggregate and the flower-like micro-architectures can be found. As illustrated in Fig.3, these flakes are made of nano-particles, which may be considered as the Y_2O_3 crystal nucleus. This is also popularly explained as the first stage of the formation of other crystal nuclei[13]. Tiny nano-particles are assembled automatically to be "flakes" and then assembled again to form initial flower-like structures. For Y_2O_3:5%Eu^{3+},24%Li^+ sample as shown in Fig.3f, most of the nano-flakes are aggregated each other and no discrete single nano-flakes can be found. With increasing Li concentration, more and more flowers appear, and the flowers also become bigger and bigger as presented in Fig.3.

The excitation spectra (Fig.4a) monitored at 613 nm exhibit sharp excitation lines of the Eu^{3+} ions, in the longer wavelength region (at 398, 468, and 538 nm). It is attributed to the direct absorption of the Eu^{3+} ion assigned to transitions of $^7F_0 \rightarrow {}^5L_6$, $^7F_0 \rightarrow {}^5D_2$, and $^7F_1 \rightarrow {}^5D_1$, respectively. The emission spectra of Y_2O_3:Eu^{3+} (5%), Li^+ (x%)($0 \le x \le 24$) film are given in Fig.4b. The spectra are composed of the well-known lines locating at 598 nm($^5D_0 \rightarrow {}^7F_4$), 618 nm ($^5D_0 \rightarrow {}^7F_2$), and 650 nm($^5D_0 \rightarrow {}^7F_3$) upon excitation with 398 nm irradiation. Similar phenomenon has been reported in other Eu^{3+}-activated red-emitting phosphors [14]. The emission intensity are enhanced with the increasing of Li^+ doped content and reaches the highest intensity at x=15, and then gradually decreases with further increase of Li concentration. That is to say, the optimal Li^+ doped content in Y_2O_3:Eu^{3+}(5%), Li^+ (x%) ($0 \le x \le 24$) phosphor is x=15.

Fig.5 shows the FT-IR spectra of x=0, 6, 12, 15, 18, and 21 samples. The peaks in the range 1380~1500 cm^{-1} and around 3500 cm^{-1} are assigned to the bending modes and the stretching modes of OH^- groups, respectively [15]. As can be seen from these spectra, the intensity of all impurity peaks becomes weaker when adding Li^+ ions into Y_2O_3:Eu^{3+}(5%), Li^+ (x%) ($0 \le x \le 24$) compounds. It indicates that the enhanced photoluminescence intensity may also result from the reducing number of OH^- groups. Since the OH^- groups with high vibration frequency can increase the non-radiative relaxation rate and hence decrease photoluminescence efficiency[4]. The reduced OH^- group absorption, as discussed in Fig.5, means the reduction of the OH^- groups decreases the non-radiative transition probability with Li^+ doping. On the other hand, the incorporation of Li^+ ions creates the oxygen vacancies, which might act as one sensitizer for the effective energy transfer due to the strong mixing of charge transfer states[16]. The oxygen vacancies in the surface of the nano-crystals will decrease the luminescence quenching centers and increase the crystallinity, thereby enhancing the emission intensity. With the gradual increase in Li^+ content, the oxygen vacancies of the host lattice greatly increase, which will destroy the emission intensity. So the intensity of photoluminescence will be reinforced as the Li^+ concentration increases from 0% to 15%, and then decline as the Li^+ concentration increases further.

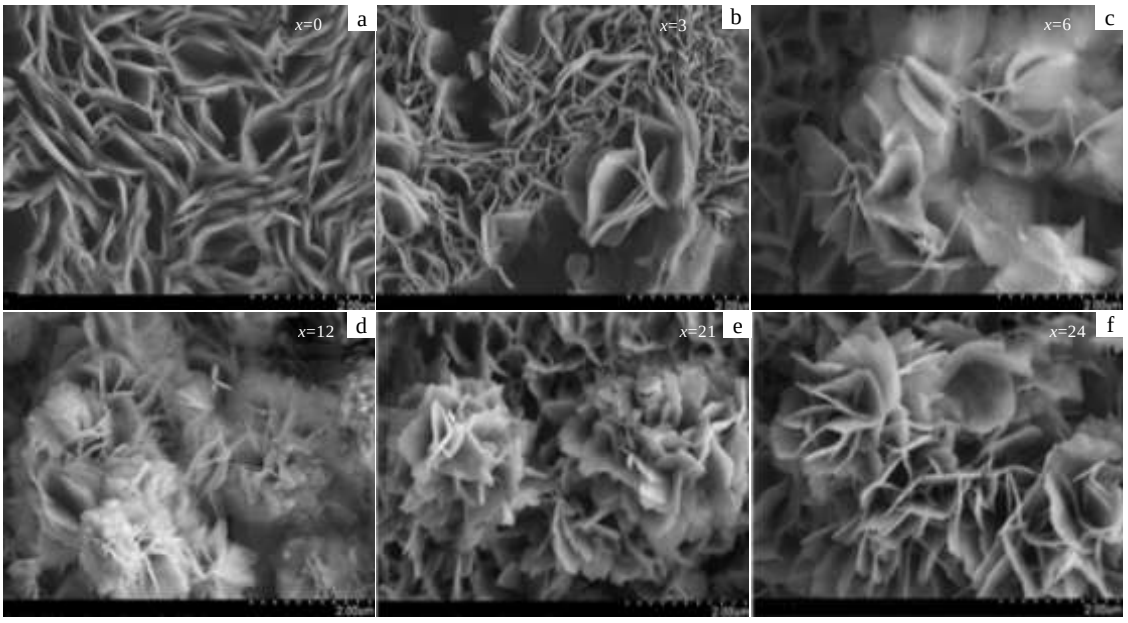

Fig.3 SEM images for Y_2O_3:5%Eu^{3+} (a), Y_2O_3:5%Eu^{3+}, 3%Li^+ (b), Y_2O_3:5%Eu^{3+}, 6%Li^+ (c), Y_2O_3:5%Eu^{3+}, 12%Li^+(d), Y_2O_3:5%Eu^{3+}, 21%Li^+ (e), and Y_2O_3:5%Eu^{3+}, 24%Li^+ (f)

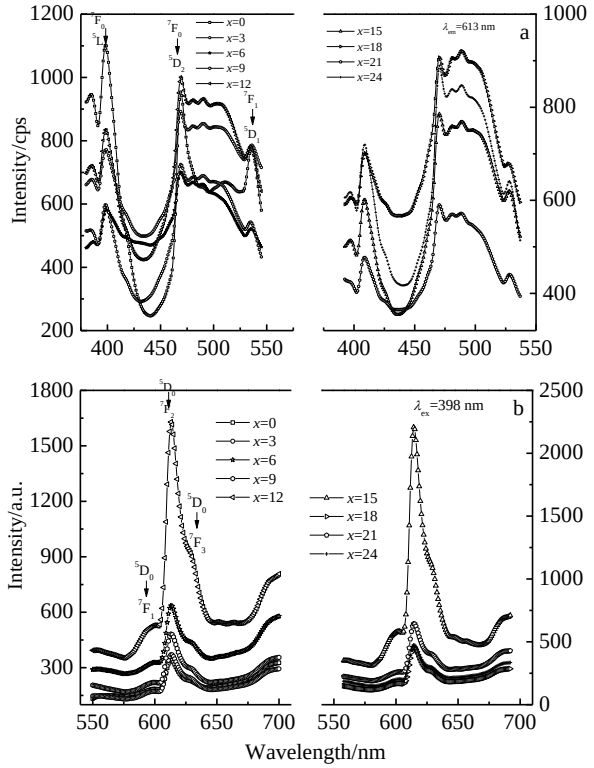

Fig.4 Excitation spectra (λ_{em}=613 nm) (a) and emission spectra (λ_{ex}=398 nm) (b) for Y_2O_3:5%Eu^{3+}, x%Li^+ ($0 \le x \le 24$) film

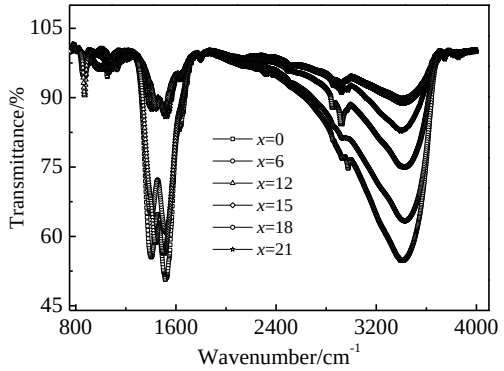

Fig.5 FI-TR spectra for Y_2O_3:5%Eu^{3+}, x%Li^+ (x=0, 6, 12, 15, 18, and 21) samples

In Fig.6, it is shown that the decay behaviors of the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} (λ_{em}=613 nm) for Y_2O_3:5%Eu^{3+}, x%Li^+ (x=0, 12, and 24) samples are excited at 398 nm. All these experimental curves can be well fitted as single exponential functions. The lifetime values are also shown in Fig.6.

2.2 Effect of deposition reaction time on the morphology and luminescent properties of Y_2O_3: 5%Eu^{3+}, 21%Li^+

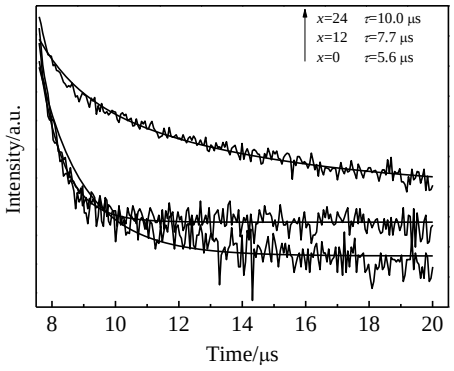

Fig.6 Decay lifetime spectra for the $^5D_0 \rightarrow {}^7F_2$ transition of Y_2O_3:5%Eu^{3+}, x%Li^+ (x=0, 12, and 21) samples

To investigate the growth mechanism of such flower-like nano-structures further, we take the Y_2O_3:5%Eu^{3+}, 21%Li^+ as an example to investigate the effect of different electro-deposition time on the micro-morphology and luminescent properties.

In the current study, cell reactions occurring with the applied electric field are as follows:

$Y(NO_3)_3+H_2O \rightarrow Y^{3+}+NO^{3-}$

$Eu(NO_3)_3+H_2O \rightarrow Eu^{3+}+NO^{3-}$

$LiNO_3+H_2O \rightarrow Li^{+}+NO^{3-}$

$NO^{3-}+H_2O+2e^- \rightarrow NO^{2-}+2OH^-$

$Y^{3+}+Eu^{3+}+Li^{+}+OH^- \rightarrow Y(OH)_3+Eu(OH)_3+LiOH$

$Y(OH)_3+Eu(OH)_3+LiOH \rightarrow Y_2O_3$:Eu,Li

After the electric potential was applied on the cell, the free Y^{3+}, Eu^{3+}, and Li^+ ions in the solution would be moved toward the cathode (ITO substrate) and condensed to Y, Eu, and Li droplets. These Y, Eu, and Li droplets reacted with hydroxide to form $Y(OH)_3$, $Eu(OH)_3$ and LiOH. The amount of Y^{3+}, Eu^{3+}, and Li^+ ions, which are condensed on the ITO glass, increased with delaying the deposition time. As a result, the diameter and shape of the nano-flower core would be increased, as shown in Fig.7. Fig.7a, 7b, and 7c present the SEM morphologies for the deposition time of 0.5, 1.0, and 1.5 h, respectively. The product is totally composed of flower-like nano-structure. After the deposition for 0.5 h as shown in Fig.7a, the products exhibit the flower-like morphology. However, comparing with the samples obtained after depositing for 1.0 h and 1.5 h, these flowers are less and irregular. As the deposition time has proceeded for 1 h, the sample exhibits totally flower-like morphology, except that only some smaller flowers exist as shown in Fig.7b. Fig.7c is the sample for the deposition time of 1.5 h, and the sample is totally composed of the uniform nano-flowers. Based on the time-dependent experiment, a so-called three step process was proposed for the formation of the flower-like nano-structure[17].

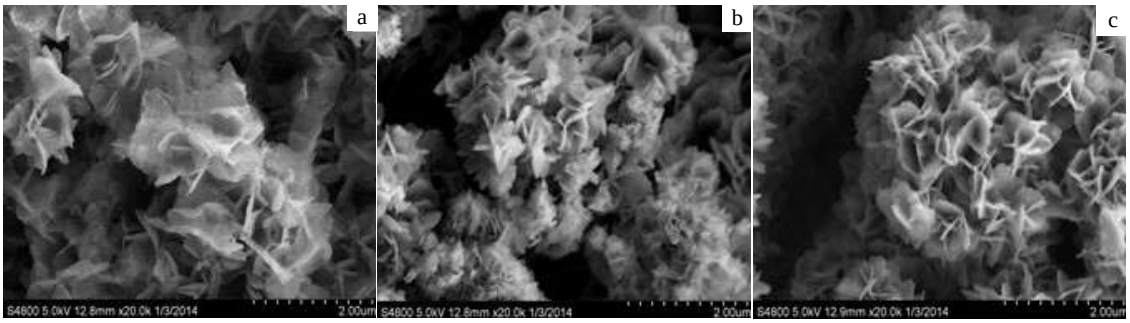

Fig.7 SEM morphologies of Y_2O_3:5%Eu^{3+}, 21%Li^+ for different deposition time: (a) 0.5 h, (b)1.0 h, and (c)1.5 h

The emission spectra of Y_2O_3:5%Eu^{3+}, 21%Li^+ with different deposition time were also studied. The obtained results are presented in Fig.8. Obviously, the emission intensity is enhanced with the increasing of deposition time. This suggests that more Eu^{3+} ions are deposited in Y_2O_3:Eu^{3+}(5%), Li^+(21%) thin film. The variation of emission intensity with the deposition time may be related to the micro-structure during the growth process as shown in Fig.7. The highest emission intensity grown for 1.5 h deposition has the largest and the most regular nano-flower.

2.3 Effect of concentration of the solution on the morphology and luminescent properties of Y_2O_3: 5%En^{3+}, 24%Li^+

Fig.9a and 9b present the SEM images of the obtained samples Y_2O_3:5%Eu^{3+}, 24%Li^+ when the concentration of solution is 0.08 and 0.10 mol/L, respectively. In the solution, higher solution concentration means more particles, resulting in the adequate growth of the nano-flakes and the aggregation of the flowers. The emission intensities of 0.08 and 0.10 mol/L of Y_2O_3:5%Eu^{3+}, 24%Li^+ film are shown in Fig.10. Obviously, in the case of higher concentration solution with more particles, the stronger emission intensity is observed.

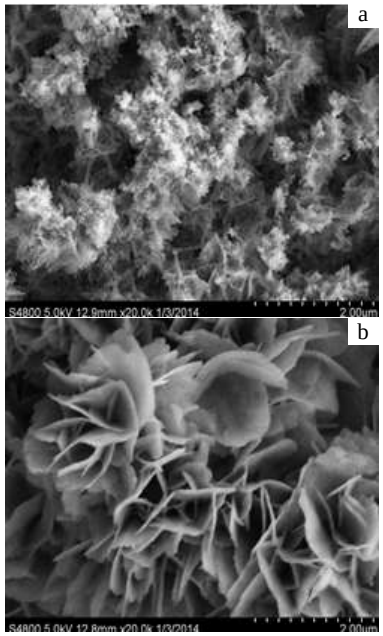

Fig.9 SEM images of Y_2O_3:5%Eu^{3+}, 24%Li^+ film for different concentrations of solution: (a) 0.08 mol/L and (b) 0.10 mol/L

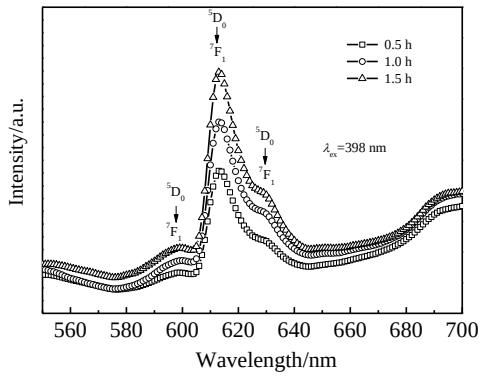

Fig.8 Emission spectra of Y_2O_3:5%Eu^{3+}, 21%Li^+ for different deposition time

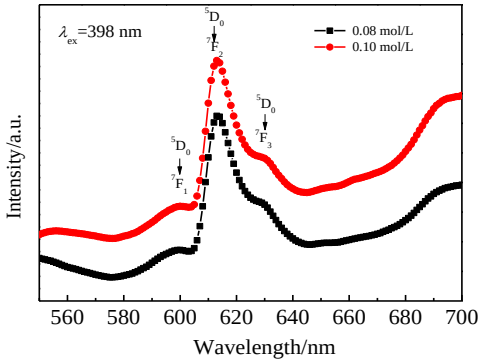

Fig.10 Emission intensity of Y_2O_3:5%Eu^{3+}, 24%Li^+ film for different concentrations of solution

3 Conclusions

1) Y_2O_3: 5%Eu^{3+}, *x*% Li^+ phosphor thin film can be prepared by electro-deposited method. Doped Li^+ ions do not change the structure of Y_2O_3:Eu^{3+}. The samples are composed of a large number of uniform nano-structure flakes. With Li doping, the flakes aggregate gradually and the flower-like micro-architectures are observed.

2) The emission intensity is enhanced with Li doping level increasing from 0 to 15%, and then declines with Li doping further.

3) The deposition time and solution concentration are also important factors determining the morphology and the emission intensity of Y_2O_3: 5%Eu^{3+}, *x*%Li^+ thin film.

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Li 含量、沉淀时间以及溶液浓度对 Y_2O_3: 5%Eu^{3+}, *x*%Li^+ 薄膜的形貌和光学性能的影响

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摘 要：利用电化学沉积法制备 Li 掺杂的 Y_2O_3: 5%Eu^{3+}, *x*% Li^+荧光薄膜，并且研究了 Li 含量，沉积时间和溶液浓度对样品的表面形貌和发光强度的影响。结果表明，上述三者对所制备的 Y_2O_3: 5%Eu^{3+}, *x*% Li^+荧光发光薄膜的形貌和发光性能均有影响。并且当 *x*=15 时，样品的形貌和发光强度表现最佳。

关键词：荧光发光薄膜；电化学沉积；Li 离子掺杂

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