平面光波導元件之鉺共摻雜氧化鈦基薄膜材料製程與光電特性研究

Physical characteristics and optical properties of sol-gel derived Er^{3+}-Yb^{3+} codoped TiO_2 for optical waveguide

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中文摘要

本研究主要是在探討氧化鈦材料來當作母材的鉺、鐿共摻雜氧化鈦薄膜，其藉由鐿離子的共摻雜，將使得此薄膜所放射出的~1.54 μm 螢光的發光強度較現今被廣泛報導且具有良好螢光特性的鉺、鋁共摻雜氧化矽薄膜的螢光強度還強約 17 倍，且此螢光頻譜的半高寬亦增寬約 1.4 倍，此外，同時此薄膜亦具有較低的製程溫度(比鉺、鐿共摻雜氧化矽之製程溫度低~300°C)，故其可應用在積體光學中平面光波導放大器的製作上。

關鍵詞: 鉺、鐿共摻雜氧化鈦、螢光、溶凝膠、分散性

Abstract

Er^{3+}-Yb^{3+} codoped TiO_2 films were prepared on fused silica by sol-gel processes. The maximum ~1.54 μm photoluminescence (PL) intensity occurs in the Er^{3+} (5 mol %)-Yb^{3+}(30 mol %) codoped TiO_2 samples annealed at 700 °C. However, when the concentration of Yb^{3+} ions attends to 50 mol %, the back energy transfer effect from Er^{3+} to Yb^{3+} will deteriorate the ~1.54 μm PL efficiency. It was believed that the Yb^{3+} ion does not only play a disperser but also a sensitizer to Er^{3+} ion. This dual effects lead to the larger PL intensity in Er^{3+}-Yb^{3+} codoped TiO_2 system than that in Er^{3+}-Y^{3+} codoped TiO_2 system. Even compared with the SiO_2 films with Er^{3+} (3 mol %)-Yb^{3+} (30 mol %) codoped and annealed at an optimal temperature of 985 °C, the Er^{3+}-Yb^{3+} codoped TiO_2 film can obtain better PL properties at a lower annealing temperature.

Key words: Er^{3+}-Yb^{3+} codoped TiO_2 、photoluminescence、sol-gel、dispersion

1. Introduction

TiO_2 film has higher refraction index (n=2.52 for anatase and n=2.76 for rutile) as well as lower phonon energy (<700 cm^{-1})[1] than silica glass film, Er^{3+}-doped TiO_2-based films have shown potential applications in the micro-integrated photonic devices. However, little detailed studies were made to investigate the role of Er^{3+} content in the PL properties of Er^{3+}-doped TiO_2 films.[2,3]

TheYb^{3+} codopant has been demonstrated in increasing the variation of Er sites that results in the inhomogeneous broadening effect.[4] In addition, Yb^{3+} ion can sensitize Er^{3+} ions so as to enhance the ~1.54 μm PL intensity.[5] However, the role of Yb^{3+} ion in phase development and related optical properties of Er^{3+}-doped TiO_2 system has been not investigated. Furthermore, Yb^{3+}/Y^{3+}/Er^{3+} ions have similar ionic radii (Yb^{3+} = 0.0862, Y^{3+} = 0.0892, and Er^{3+} = 0.0881 nm) and Yb_2O_3/Y_2O_3/Er_2O_3 have nearly the same crystal structural and lattice constant.

Therefore, it is very important to investigate the influence of co-dopant Yb^{3+} on the physical characteristics and optical properties of Er^{3+}-doped titania. Furthermore, the role of Yb^{3+} and Y^{3+} codopants in photoluminescence properties of Er^{3+}-doped titania materials will be discussed and compared.

2. Experimental

A. Thin films preparation

The Er^{3+}-Yb^{3+} codoped TiO_2 films were prepared from yttrium acetate, erbium acetate (Alfa) and titanium isopropoxide. The as-deposited films were first pyrolyzed under dry oxygen atmospheres at 400 °C for 30 min and then annealed at 600-1000 °C for 1 h in dry oxygen atmosphere.

B. Characterization measurements

The phase structures of films were analyzed by X-ray diffractometer. The electron spin resonance (ESR) spectra were recorded using a Bruker ESR spectrometer. The fluorescence spectra were excited by a 980 nm diode laser. Erbium L_{III}-edge X-ray absorption spectra were recorded at Synchrotron Radiation Research Center (SRRC), Hsinchu.

3. Results and discussion

3.1. Structural evolution

The X-ray diffraction (XRD) patterns in Fig. 1(a) show the effect of annealing temperatures on structural evolution of Er^{3+} (5 mol %)-doped TiO_2. It is obvious that the addition of more than 5 mol %

Er^{3+} ions can lead to the destruction of TiO_2 network structure. The crystallinity of anatase TiO_2 was reduced and anatase-to-rutile (A → R) transformation rate was accelerated (e.g., the anatase phase totally disappear at 900 °C annealing). Additionally, the $Er_2Ti_2O_7$ pyrochlore phase (P) was detected at 800 °C. For the Er^{3+} (5 mol %)-Yb^{3+} (30 mol %) codoped TiO_2 samples, the XRD patterns in Fig. 1(b) show that when the samples were annealed 700 °C, the host matrix becomes amorphous for Yb^{3+} concentration above 10 mol %. Additionally, Yb^{3+} codopant was found to accelerate the A→R transformation; all of the anatase phase has been transformed into rutile phase at 800 °C. After the Er^{3+}-Yb^{3+} codoped TiO_2 samples were annealed at 900-1000 °C, both rutile (R) and pyrochlore (P) phase become more well-crystallized. Similar results are also observed in the Y^{3+}-doped TiO_2 system.

In addition, Fig. 2 shows the surface morphologies of Er^{3+}-doped TiO_2 and Er^{3+}-Yb^{3+} codoped TiO_2 samples annealed 700°C/1 h. The grain sizes of the TiO_2 samples doped with Er^{3+} (5 mol %), Er^{3+}-Yb^{3+} (5-10 mol %) are about 60 and 25 nm, respectively. It has been well known that smaller grains can provide more surface nucleation sites, which can accelerate the A → R phase transformation. Therefore, the smaller grain size in Er^{3+}-Yb^{3+} codoped TiO_2 samples than Er^{3+}-doped TiO_2 samples reflects the higher A → R transformation rate.

Figure 3 shows the pseudo-radial distribution functions obtained from the k^3-weighted Fourier transforms of the Er^{3+}-Yb^{3+} codoped TiO_2 samples annealed at 700 for 1 h. Qualitative observation of the 700°C-annealed samples (i.e., no formation of pyrochlore phase) reveals that the first and second-neighbor distance around Er^{3+} is close to the Er-O and Er-Er bond length of Er_2O_3, respectively. This means that the local structure around Er^{3+} ions in the Er^{3+}-Yb^{3+} codoped TiO_2 systems is similar to that of the crystalline Er_2O_3. Additionally, it is noted that the second-neighbor distance around Er^{3+} slightly increased with the increase of Yb^{3+} concentration up to 30 mol%. The increased second-neighbor distance seems to reveal that the second shell may partially contain Yb^{3+} ions. This phenomenon can be attributed to the fact that as Er^{3+} and Yb^{3+} have the same valence and close ionic radii, they can be replaced with each other. However, as the Er^{3+}-doped TiO_2 was codoped with 50 mol% Yb^{3+}, the second-neighbor distance around Er^{3+} becomes larger as compared to that with 30 mol% Yb^{3+} codoped that is probably due to a high disorder around Er^{3+} ions.

3.2. ~1.54 μm photoluminescence properties

Figure 4 shows the ~1.54 μm PL spectra of the Er^{3+} (5 mol %)-doped TiO_2 samples with 0-50 mol % Yb^{3+} added and annealed at 700 °C for 1 h. All of the spectra were normalized to the same intensity to compare the difference between spectral features. The Er^{3+} (5 mol %)-doped TiO_2 sample exhibits a sharp PL spectrum with a 1.537 μm main peak which is characteristic emission ($^4I_{13/2} \rightarrow {}^4I_{15/2}$) of Er^{3+} ion. However, by increasing the Yb^{3+} codopant concentration, the PL spectra became more broaden. The maximum bandwidth (FWHM= 67 nm) of ~1.54 μm PL spectra was obtained for the sample added with Yb^{3+} content above 30 mol %. The line-broadening mechanism can be attributed to the inhomogeneously broadened transition of Er^{3+} ions.[6] For the sample without Yb^{3+} codopant, the well-resolved spectrum demonstrates that the Er^{3+} ions are located in well-defined sites of TiO_2 matrix. Namely, each Er^{3+} ion occupies the similar type of site that has well-defined surrounding and hence each Er^{3+} ion experiences the similar crystal field. However, the Yb^{3+} codopant can destroy the network of TiO_2 host matrix, which results in the varying Er sites with different surrounding environment and causes a randomization of the Stark splittings. Therefore, the overall spectral lines resulting from the superimposed contributions of each Er site are inhomogeneously broadened.

Figure 5 illustrates that the influence of annealing temperatures on the ~1.54 μm PL spectral feature of Er^{3+}(5 mol%)-Yb^{3+}(30 mol%) codoped TiO_2 samples. The higher annealing temperature (≧800 °C) leads to the spectra with many splitting lines. From the XRD detection, it shows that the $Er_2Yb_{2-x}Ti_2O_7$ crystallites were generated at the annealing temperatures above 800 °C. This means that the majority of Er^{3+} ions should be located in the crystalline $Er_2Yb_{2-x}Ti_2O_7$ phase and the Er^{3+} bonding environment becomes uniform to produce the well-resolved PL spectrum.

The variation of the ~1.54 μm PL intensity of Er^{3+}-Yb^{3+} codoped TiO_2 samples with Er^{3+}-Yb^{3+} concentration was summarized in Fig. 6. By codoping 10-30 mol % Yb^{3+} ions into Er^{3+}-doped TiO_2 samples, the PL intensity can be remarkably enhanced. Nevertheless, the 50 mol % Yb^{3+} codopant leads to the reduction of PL intensities that might be related to the back energy transfer from Er^{3+} to Yb^{3+} ions[6] and the double energy transfer (DET). For comparison, the Er^{3+}(5 mol%) -Yb^{3+}(30 mol%) codoped silica film was also prepared and annealed at an optimal temperature of ~ 985°C. Figure 7 illustrates that the PL properties of the Er^{3+}-Yb^{3+} codoped TiO_2 system exhibit more intense emission (~2 times) and wider FWHM

(~1.5 times) than those of optimal Er^{3+}-Yb^{3+} codoped SiO_2 system. This result implies that the PL properties strongly depend on the composition and structure of the host materials. Furthermore, the Er^{3+}-Yb^{3+} codoped TiO_2 film does not only obtain better PL properties but also lower annealing temperature.

The dependence of annealing temperatures on the PL intensities of Er^{3+} (5 mol %)-Yb^{3+} (30 mol %) codoped TiO_2 samples were shown in Fig. 8. The increase in PL intensity from 600 to 700 ^oC is attributed to the reduction of OH^- hydroxyl content (as one can see in Fig. 9, the decrease of FTIR absorption around 4000-3000 cm^{-1} corresponding to the O-H vibration mode increases with the annealing temperature.).[7] However, above 800 ^oC, the PL intensity is abruptly reduced that is strongly related to the formation of pyrochlore phase. The $Er_xYb_{2-x}Ti_2O_7$ pyrochlore crystallites as identified from XRD patterns are generated at 800 ^oC and its crystallinity can be enhanced at higher temperature annealing. Therefore, the local structure around Er^{3+} ions in the well-crystallized $Er_xYb_{2-x}Ti_2O_7$ phase becomes higher-order symmetry compared to that of Er^{3+} ions in amorphous host matrix. That results in the reduced probability of the normally forbidden intra-4*f* transition of Er^{3+} ions and the degradation in the PL efficiency.[8]

On the other hand, for the Er^{3+}-doped TiO_2 sample codoped with Y^{3+}, the ~1.54 μm PL spectra (no shown here) exhibit the similar effects to the Er^{3+}-Yb^{3+} codoped TiO_2 samples. An enhancement of PL intensities with increasing Y^{3+} content was observed for the Er^{3+} (5 mol %)-Y^{3+} (10-50 mol %) codoped TiO_2 samples as shown in Fig. 10. In contrast, a maximum PL intensity appears at the sample of Er^{3+} (5 mol %)-Yb^{3+} (30 mol %) codoped TiO_2, above that, a reduced PL intensity was observed such as for the sample with 50 mol% Yb^{3+}. As comparing the PL intensities of TiO_2 samples codoped with Er^{3+} (5 mol %)-Yb^{3+} (30 mol %) with Er^{3+} (5 mol %)-Y^{3+} (30 mol %), it demonstrates that the PL intensity in the former is about ~ 2 times higher than that in the latter. According to the aforementioned experimental results, the mechanisms for the enhancement of PL intensity between Yb^{3+} and Y^{3+} codoping are somewhat different.

For the Er^{3+}-Y^{3+} (or Er^{3+}-Yb^{3+}) codoped TiO_2 systems without the formation of pyrochlore phase (i.e., the annealing temperature $\leqq$ 700 ^oC), the EXAFS analysis (see Fig. 3) shows that the local environment of Er sites is similar to Er_2O_3 in host matrix. We believe that the Er sites with Er_2O_3-like environment are optically active centers as the case in the Er^{3+}-doped silicate glasses.[9] Because Er^{3+} and Yb^{3+} (or Y^{3+}) have the same valence and similar ionic radii, they could be replaced with each other and the -Er-O-Er-O-Er- bonding structures can be changed into -Er-O-[Yb (or Y^{3+})-O]$_n$-Er-. Therefore, the more Y^{3+} codopant results in the larger atomic spacing among Er^{3+} ions and the enhanced PL properties that can be attributed to the increased dispersion and solubility of Er^{3+} ions in Er^{3+}-Yb^{3+} (or Er^{3+}-Y^{3+}) codoped TiO_2 systems. However, it is worthy to note that with increasing Yb^{3+} up to 30 mol%, the PL intensity was remarkably enhanced. It implies that the Yb^{3+} ion does not only play a disperser but also a sensitizer to Er^{3+} ion. This dual effects might have the superimposed impact to the ~1.54 μm PL efficiency, which seems consistent with our experimental results that the Er^{3+}-Yb^{3+} (10-30 mol %) codoped TiO_2 samples have larger PL intensity than that of Er^{3+}-Y^{3+} (10-30 mol %) codoped TiO_2 samples.

4. Conclusions

(1) The maximum ~ 1.54 μm PL intensity was obtained for the Er^{3+} (5 mol %)-Yb^{3+} (30 mol %) codoped TiO_2 sample and annealed at 700 ^oC. This can be attributed to the competition between the content of hydroxyl groups and Er site symmetry. Below 700 ^oC, the content of hydroxyl groups plays an important role in PL intensity. On the other hand, above 700 ^oC, the formed pyrochlore phases in the Er^{3+}-Yb^{3+} codoped TiO_2 systems can result in the degradation of ~1.54 μm PL efficiency and the formation of well-resolved spectral lines.

(2) The local chemical environment of Er^{3+} ions in Er^{3+}-Yb^{3+} codoped TiO_2 films is similar to that in Er_2O_3 and the average spatial distance between Er^{3+} ions is slightly increased due to the partial substitution of Yb^{3+} for Er^{3+} ions in the Er_2O_3-like local structure. That indicates that Yb^{3+} ion can act as disperser to Er^{3+} ions and reduce the concentration quenching effect.

(3) In comparison with the Er^{3+}-Y^{3+} codoped TiO_2 samples, the Yb^{3+} ion in the Er^{3+}-Yb^{3+} codoped TiO_2 samples does not only play a disperser but also a sensitizer to Er^{3+} ion. This dual effects lead to the larger PL intensity in Er^{3+}-Yb^{3+} codoped TiO_2 system than that in Er^{3+}-Y^{3+} codoped TiO_2 system. However, when the concentration of Yb^{3+} ions attends to 50 mol %, the back energy transfer effect from Er^{3+} to Yb^{3+} will deteriorate the ~1.54 μm PL efficiency.

Acknowledgments

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References

1. C. Urlacher and J. Mugnier, J. Raman Spectrosc. **27**, 785 (1996).
2. A. Bahtat, M. Bouazaoui, M. Bahtat, and J. Mugnier, Opt. Commun. **111**, 55 (1994).
3. A. Bahtat, M. Bouderbala, M. Bahtat, M. Bouazaoui, J. Mugnier, and M. Druetta, Thin Solid Films **323**, 59 (1998).
4. C. C. Robinson and J.T. Fournier, J. Phys. Chem. Solids **31**, 895 (1970).
5. E. Cantelar and F. Cussó, Appl. Phys. B **69**, 29 (1999).
6. E. F. Artemev, Sov. J. of Quant. Electr. **11**, 1266 (1981).
7. R. F. Bartholomew, B.L. Butler, H.L. Hoover, and C.K. Wa, J. Am. Ceram. Soc. **63**, 481 (1980).
8. B.A. Block and B.W. Wessels, Appl. Phys. Lett. **65**, 25 (1994).
9. M. Marcus, D. Jacobson, A. Vredenberg, and G. Lamble, J. Non-Cryst. Solids **195**, 232 (1996).

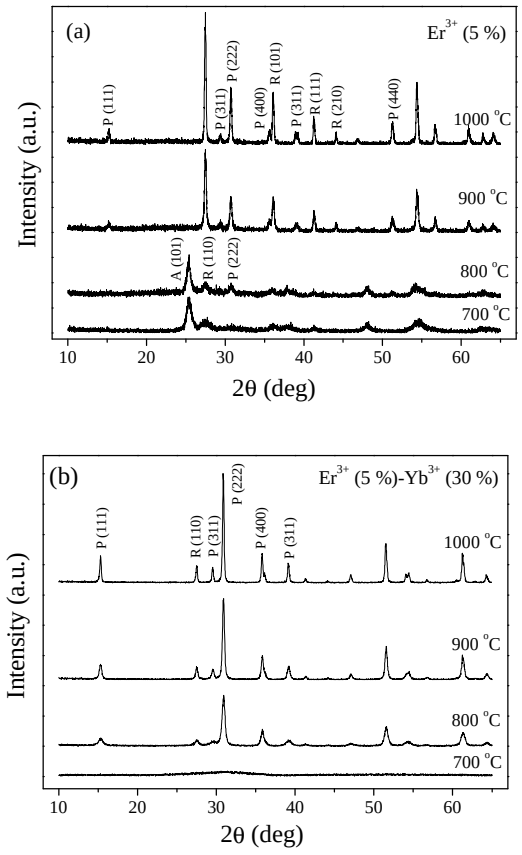

Fig. 1. XRD patterns of (a) Er^{3+}-doped TiO_2 and (b) different Er^{3+}-Yb^{3+} codoped TiO_2 films annealed at 700-1000 °C for 1 h.

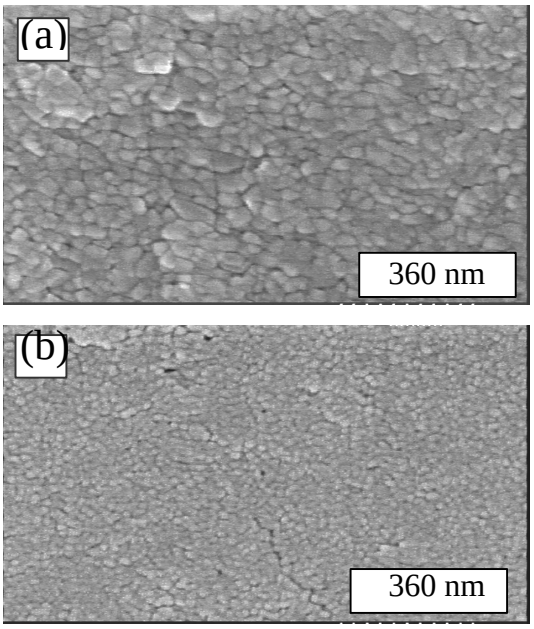

Fig. 2. Dependence of various Er^{3+}-Y^{3+} codoped TiO_2 Films at 700°C on refractive index.

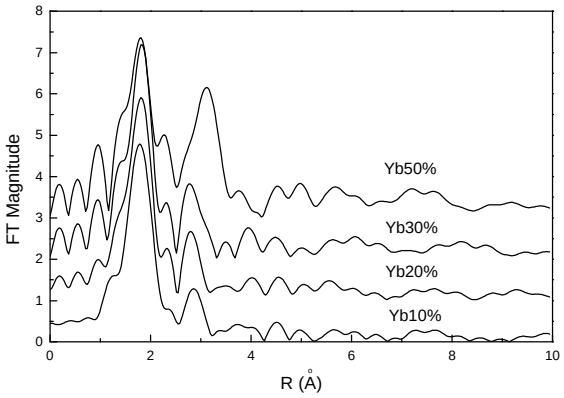

Fig. 3 Fouier transform of EXAFS function at Er L_{III}-edge for the samples annealed at 700 ℃ with various Yb content.

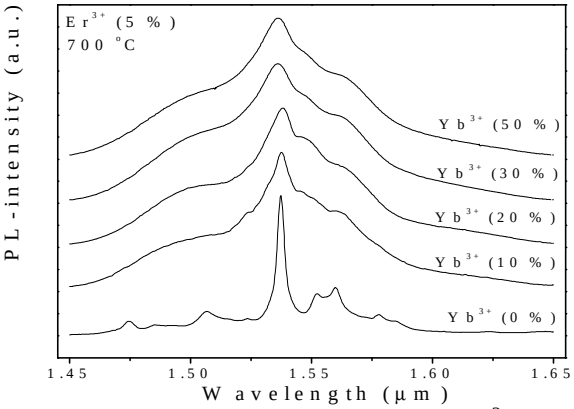

Fig.4 ~1.54 μm PL spectra of the Er^{3+} (5 mol %)-doped TiO_2 samples with 0-50 mol % Yb^{3+} codopant annealed at 700 °C for 1 h.

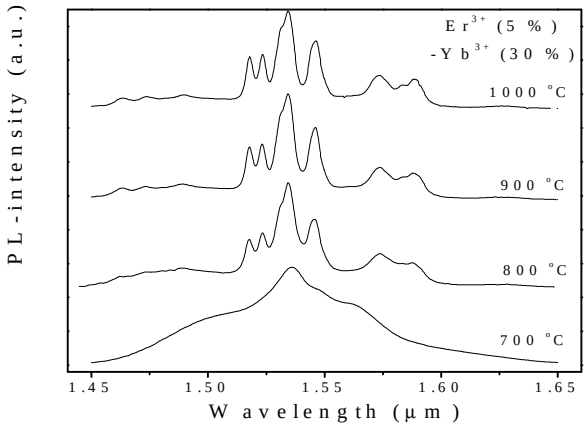

Fig. 5 ~1.54 μm PL spectra of theEr^{3+} (5 mol %)-Yb^{3+} (30 mol %) codoped TiO_2 annealed from 700 to 1000 ^oC for 1 h.

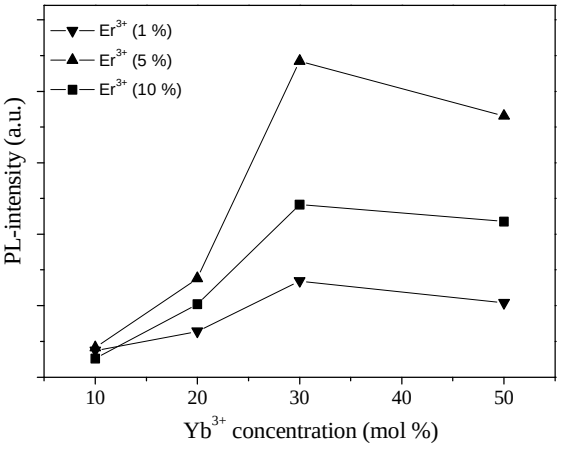

Fig. 6. Dependence of Yb^{3+} concentration on the ~1.54 μm PL intensity of Er^{3+}-Yb^{3+} codoped TiO_2 samples added with different concentration of Er^{3+} ions and annealed at 700 ^oC/1 h.

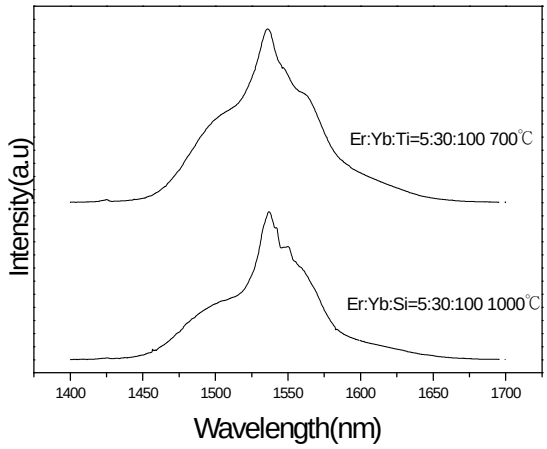

Fig. 7 PL intensity of the Er^{3+} (5 mol %)-doped TiO_2 samples with the 30 mol % Yb^{3+} codopant annealed from 600 to 1000^{o}C for 1 h.

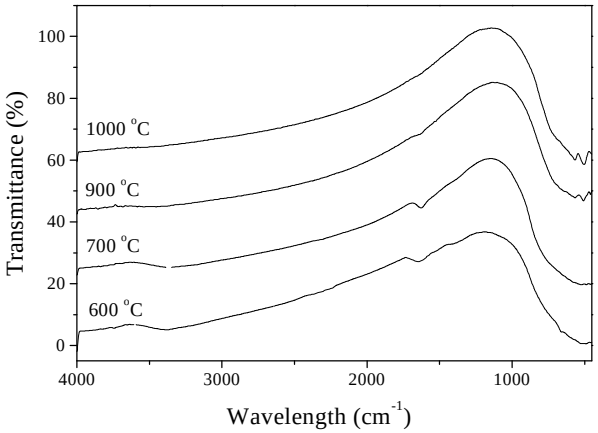

Fig. 8 Comparison of ~1.54 μm PL spectra of Er^{3+} (5 mol %)-Yb^{3+} (30 mol %) codoped TiO_2 and SiO_2 films.

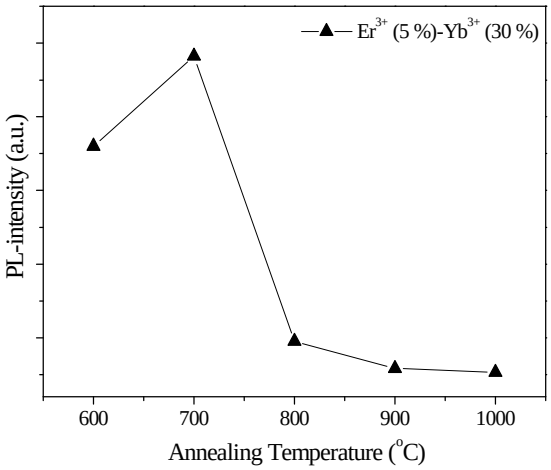

Fig. 9. FTIR transmittance spectra of Er^{3+} (5 mol %)-Yb^{3+} (30 mol %) codoped TiO_2 annealed from 600-1000 ^{o}C.

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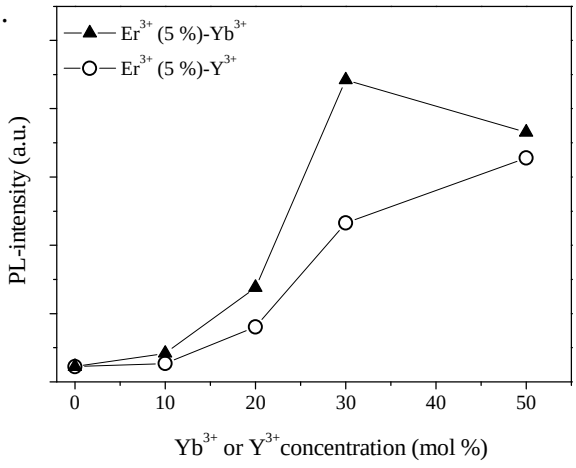

Fig. 10 Comparison of ~1.54 μm PL intensities between Er^{3+} (5 mol %)-Yb^{3+} (10-50 mol %) and Er^{3+} (5 mol %)-Y^{3+} (10-50 mol %) codoped TiO_2 system annealed at 700 ^{o}C for 1 h.