Enhanced Photoluminescence of Tb³⁺ Ions Ce³⁺ Ions and SnO₂ Nanocrystals Co-doped Silica Thin Films

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Abstract

Co-doping Ce^{3+} ions and size-tunable SnO_2 nanocrystals into Tb^{3+} ions embedded silica thin films produces a ninefold enhancement of Tb^{3+} related emission. Firstly, by optimizing the doping ratio of Sn^{4+} ions, the size of SnO_2 nanoparticles was well tailored for achieving a greatly enhanced photoluminescence emission from Tb^{3+} ions. Another method to significantly enhance Tb^{3+} emission was increasing the proportion of Ce^{3+} , and this method only require a relatively small amount rare earth (RE) ions for obtaining an obvious emission enhancement. On the other side, companied with the increase of Ce^{3+} ions concentration, the growth of CeO_2 nanoparticles were proved seriously attenuated the photoluminescence intensity of Tb^{3+} ions. Finally, we also analyzed the influence of annealing temperature on the photoluminescence intensity. These results indicated that an appropriate proportion of Ce^{3+} ions and suitable size of SnO_2 nanocrystals can effectively sensitize the luminescence of Tb^{3+} ions.

1. Introduction

The design and manufacture of silicon-based light sources, are main challenges in modern optoelectronics^[1–3]. Now researchers are trying to dope different light-emitting centers into a precursor, and then cover the silicon substrate in the form of thin film to obtain different silicon-based light sources. Sol-gel method is one of the most commonly used methods. As a wet chemical technology, the sol-gel method can produce high purity glass at temperatures below the melting point and allows incorporation of much higher concentration of dopants than the melt process^[4–6]. Because of its good physical properties and chemical stability, sol-gel method has been widely used in the research of silicon-based light sources with rare earth ions as dopants, such as Trivalent terbium^[7]. Therefore, the silicon-based luminescent film doped with Tb^{3+} made by the sol-gel method has good potential as an effective green light emissive center. Despite Tb^{3+} ions being good green light emissive center, its f-f electronic transitions are parity forbidden, so that direct 4f excitation with conventional light sources normally yields only weak luminescence^[8].

Many researchers are trying to improve the emission efficiency of terbium with other rare earth ions through various methods. O.M. Ntwaeaborwa et al. prepared Ce^{3+} ions and Tb^{3+} ions powder phosphors by the sol-gel method. Blue emission from the Ce^{3+} ions was completely suppressed by Tb^{3+} ions co-doping, in the meantime the luminous intensity of Tb^{3+} ions was greatly enhanced^[9]. Yagoub M Y A et al. believe that the overlap occurred between emission band of Ce^{3+} and several of the Tb^{3+} 4f-4f excitation bands meets the requirement for the energy transfer between these two RE ions^[10]. Morais Faustino B M et al. produced SnO_2 nanoparticles doped with a range of lanthanide ions (Ln^{3+}) by sol-gel method. It is also found that nanoparticles of SnO_2 can effectively sensitize the emission of some RE ions^[11]. Zhang X

et al. proposed that the effective sensitization process can be realized because of the suitable spectral overlap between the defect state energy level of SnO_2 nanoparticles and the excitation level of RE ions^[12].

Our experimental results illustrated that the size of SnO_2 nanoparticles directly affects the sensitization effect of SnO_2 nanoparticles on Tb^{3+} ions^[13]. The size of SnO_2 nanoparticles prepared by sol-gel method is determined by the concentration of Sn^{4+} ions. However, a too large or too small SnO_2 nanoparticles will suppress the sensitization effect on the emission of Tb^{3+} ions, thus the density of SnO_2 nanoparticles in silicon thin films should be carefully selected after the size of SnO_2 nanoparticles is determined. To further improve the luminous efficiency of Tb^{3+} ions, we introduced another kind of RE ions Ce^{3+} , a good sensitizer for Tb^{3+} , into thin film with an appropriate doping concentration of Sn^{4+} ions. Tb^{3+} ions are simultaneously sensitized by Ce^{3+} ions and nanoparticles of SnO_2 . Spectral analysis shows that the co-sensitization effect of Ce^{3+} ions and nanoparticles of SnO_2 is much better than that of Ce^{3+} ions or nanoparticles of SnO_2 sensitized Tb^{3+} ions alone.

2. Experimental

Tb^{3+} ions, Ce^{3+} ions and SnO_2 nanoparticles co-doped silica thin films were prepared by using the sol-gel method and spin-coating technique. Tetraethyl orthosilicate (TEOS, 98%), de-ionized water and ethanol were mixed (6:1:6 in volume) as silica sol. Hydrochloric acid was then added to the mixture dropwise under rigorous stirring to adjust pH value to 2.0. Different amounts of terbium nitrate ($\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.9%) salt, cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 99.95%) salts and tin tetrachloride (SnCl_4 , 98%) were dissolved in the solution to obtain desired concentration. Then the precursor was heated to 65°C to complete hydrolysis and gelation was performed by leaving the sealed container for one day. The as-prepared gel was spin-coated onto Si substrates to form SiO_2 films followed by the post-annealing at 1000°C for one hour to eliminate hydroxyl groups (-OH), which may lead to the quenching of rare-earth-related emission as nonradiative carrier-recombination centers.

The excitation spectra, emission spectra and luminescence decay curves of the as-prepared Tb^{3+} ions and Ce^{3+} ions co-doped silica thin films were measured using an Edinburgh Instruments FLS980 fluorometer system equipped with a Xenon lamp as an excitation source. The crystal structure and orientation of the films were characterized by X-ray diffraction (XRD, Bruker D8 Advance). The XRD data were collected by using a scanning mode in the 2θ ranging from 10° to 80° with a scanning step size of 0.02°.

3. Results And Discussion

In this part, the concentrations we used in legends are all refer to molar mass concentration. Particularly, after 1000°C annealing process, the Sn^{4+} ions is oxidized into SnO_2 nanocrystals

3.1 Sensitization energy-transfer mechanism

We produced two silica thin film samples individually doped with Tb^{3+} and Ce^{3+} ions respectively and tested their PL and PLE spectrum, as shown in Figure.1. The dashes line refers to the PLE spectrum of 4% Tb^{3+} doped sample and the solid line refers to the PL spectrum of 2% Ce^{3+} samples. Obviously, there is an overlap area between these two curves, which is marked as shaded part.

Due to the existence of overlap area, the photon emitted from Ce^{3+} 5d-4f states jump is going to be absorbed by f-f transition in Tb^{3+} ions. This resonance energy transfer is believed the main factor to make the Ce^{3+} a good sensitizer for Tb^{3+} ions photoluminescence^[14, 15].

The sample of silica thin film individually doped with SnO_2 nanocrystals was tested and the PL and PLE spectrum are shown in Figure.2(a). The emission wavelength was 395nm in the excitation spectrum and the excitation wavelength was 265nm in the emission spectrum. Based on the energy state theory, we drew a band structure of SnO_2 nanocrystals to illustrate the energy transfer between oxide nanocrystals and rare earth ions, as shown in the figure.2(b). The 395nm peak in PL emission of SnO_2 is a consequence of luminescent centers in the band ($\sim 3.1\text{eV}$) gap originating from lattice defects in nanoparticles such as oxygen vacancies, Sn interstitials and surface defects, i.e. Sn-Cl or Sn-OH species^[11, 16]. As shown in the figure. 2(b), the $^5\text{D}_4$ energy level of Tb^{3+} ions is lower than the defect states of SnO_2 nanocrystals ($\sim 3.1\text{eV}$), which provides the possibility for the occurrence of energy transfer from SnO_2 nanocrystals to Tb^{3+} ions.

As shown in Figure.3, the PLE spectrum of Co-doped sample (solid line) has a strong peak near 270nm, which perfectly matches the SnO_2 excitation spectrum in Fig. 2, and this peak cannot be found in Tb^{3+} doped spectrum (dashed line). We ascribe these peak to the band-to-band transition in size-confined SnO_2 nanocrystals due to the quantum confinement effect. This phenomenon indicates that an absorption happened between SnO_2 states and the photon energy is transferred from SnO_2 nanoparticle to Tb^{3+} ions. Another small peak is observed in Tb^{3+} single doped sample near 255nm wavelength. This peak is from the $4\text{f}^8\text{-}4\text{f}^75\text{d}$ transition of Tb^{3+} and it is overlapped by broad excitation band of SnO_2 nanocrystals^[17].

3.2 Analysis of Tb^{3+} ions Ce^{3+} ions and SnO_2 nanocrystals co-doped

We selected 4% Tb^{3+} , 2% Ce^{3+} and 15% SnO_2 nanoparticles as dopants to discuss the influence of different doping strategy. As shown in Figure. 4, under the excitation of 320nm, the four PL spectra of silica thin films co-doped with different dopants all consist of four stable characterized emission peaks at 488nm, 542nm, 586nm, and 622nm, corresponding to the typical Tb^{3+} atomic energy level transitions from $^5\text{D}_4$ to $^7\text{F}_6$, $^7\text{F}_5$, $^7\text{F}_4$, and $^7\text{F}_3$, respectively. Obviously, doping of other ions has basically no influence

on the emission wavelength, which is because these four Tb^{3+} peaks are generated by f-f transitions happened on 4f orbit. As inner shell 4f orbitals are shielded by filled 5s and 5p value orbitals, these four peaks display very stable wavelength and hard to be influenced by the outside world^[7]. Therefore, the doping of Ce^{3+} ions and SnO_2 nanocrystals does not change the wavelength of Tb^{3+} ions emission peak. On the contrary, the PL emission peak of Tb^{3+} ions at 542nm was enhanced due to the sensitization of Ce^{3+} ions and SnO_2 nanocrystals. It can be seen from figure.4 that the PL emission intensity of the samples Co-doped with Tb^{3+} ions, Ce^{3+} ions and SnO_2 nanocrystals at 542nm is nine times higher than that of single doped Tb^{3+} ions. Clearly, the Ce^{3+} ions and SnO_2 nanocrystals both can enhance the emission of Tb^{3+} , and these two sensitizers can collaborate to further increase the emission intensity of Tb^{3+} ions. Therefore, in order to clarify the ability as sensitizers and their influence on PL spectrum, we choose the concentration of one sensitizer (Ce^{3+} or SnO_2 nanocrystals) as independent variable, while the other sensitizer has constant concentration as reference.

The PL emission spectra of 4% Tb^{3+} and 2% Ce^{3+} doped with SnO_2 at different concentrations are shown in Figure. 5. The graph shows a Tb^{3+} characteristic peak at 542 nm under the excitation of 320 nm UV light. When increasing Sn^{4+} concentration to 15%, the 542 nm emission intensity is gradually enhanced and reaches the peak, tripling the intensity of un-sensitized sample. If the Sn concentration is furtherly increased, the result shows a sharp descent in emission intensity, and possible reason is considered luminescent quenching effect. Figure 6 shows the XRD patterns of samples in different SnO_2 concentrations after 1000°C annealing. The wide peak that can be observed in all samples from 15° to 30° refers to amorphous silica, the matrix material. Comparing with the standard data of SnO_2 in JCPDS file 41-1445, the peaks are perfectly match the XRD pattern of Sn^{4+} , which suggest a remarkable amount of SnO_2 was generated during the annealing process. When doping 5% Sn^{4+} , there is only a very weak peak. In the case of 5% SnO_2 , the SnO_2 diffract peak is overlapped by the peak of amorphous silica and too low to detect. As the doping concentration increases, the characteristic peak of SnO_2 becomes more and more obvious. From three XRD results with SnO_2 peaks, the average values of SnO_2 crystallite size can be evaluated by using Scherrer's formula equ.1^[18, 19].

$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where D is the volume weighted crystallite size (nm); k is the shape factor ($k = 0.89$), λ is the wave length of the X-rays ($\lambda = 0.154056$ nm for Cu K α radiation); θ is diffraction angle (°) and β is FWHM. The estimated value of SnO_2 crystal sizes of three samples doped with 10%, 15% and 20% Sn^{4+} are 2.4nm, 3.7nm, 4.7nm, respectively.

Therefore, we can optimize the energy transfer efficiency by modulating the size and density of SnO_2 nanocrystals. Higher density of SnO_2 nanocrystals shortens the average distance between SnO_2

nanocrystals and Tb^{3+} ions, leading to a more effective energy transfer. When the concentration of Sn^{4+} reaches 20%, the formation size of nanocrystals increases greatly after annealing process, consequently the surface-to-volume ratio of SnO_2 nanocrystals decreases rapidly, and meantime the density of interface defects related to SnO_2 nanocrystals decreases as well, which results in the decline of photoluminescence intensity.

Here we change the independent variable to Ce^{3+} concentration, the PL emission spectra of 4% Tb^{3+} and 15% Sn^{4+} doped with Ce^{3+} at different concentrations under 320nm excitation are shown in Fig. 7. Focus on the Tb^{3+} characteristic peak about 542 nm, the intensity reaches the top when Ce^{3+} ions is 2%, and then decrease gradually with the increase of Ce^{3+} concentration. When the Ce^{3+} concentration reaches 8%, the luminescence intensity of 8% is even weaker than the sample without doping Ce^{3+} ions.

Figure.8 shows the XRD results of samples in different Ce^{3+} concentrations after 1000°C annealing. As the concentration of Ce^{3+} increases, 4 peaks at 28°, 33°, 47° and 56° become more obvious. Comparing with the standard data of CeO_2 in JCPDS file 34-0394, the four peaks are perfectly match the XRD pattern of CeO_2 , which suggest a remarkable amount of CeO_2 particles were generated during the process of annealing. This process is considered can be effectively inhibited by using reducing gas protection during annealing process. In our experiment, the samples were annealed under air phenomenon and we studied the size of CeO_2 particles generated in different concentration of Ce^{3+} samples. Naturally, the Ce^{3+} ions have the electronic configuration of the noble gas Xe plus a single 4f electron that can effectively carry out photoluminescence and energy transfer from closed 5s and 5p shells. On contrary, the Ce^{4+} ions with oxidation state are hard to cause luminescent effect or absorb energy because the last outmost electron is captured and become a stable Xe-like configuration^[20]. As a result, the mass generation of CeO_2 effectively reduced the emission intensity of Ce^{3+} and consequently hindered the energy transfer from Ce^{3+} to Tb^{3+} ions.

Based on Scherrer's formula, the size of CeO_2 particles can be calculated. The estimated results illustrate that the CeO_2 crystal sizes of the samples doped with 2%, 4%, 6%, 8% Ce^{3+} are 2.9nm, 5.7nm, 6.2nm, 7.5nm, respectively, monotonously increased with the rise of Ce^{3+} ions. Large CeO_2 nanoparticles directly destroy the energy transfer system among different particles in the sample. The most direct manifestation is that 8% Ce^{3+} ions are oxidized to CeO_2 particles about 7.5 nm during annealing. At this time, the luminescence intensity of the sample at 542 nm is weaker than that without Ce^{3+} .

Figure.9 shows the PL spectra of thin films with different temperature. With the increase of annealing temperature from 400 °C to 1000 °C, the characteristic emission intensity of Tb^{3+} ions in the co-doping samples increases obviously. We think it is caused by the following two reasons. Firstly, this increased emission intensity is attributed to the elimination of non-radiative recombination centers, -OH groups. Generally speaking, these -OH groups have relatively high characteristic phonon energy, which are common non-radiative recombination centers, which quench the luminescence of the luminescent center.

Fortunately, the existing studies show that with the increase of annealing temperature, the intensity of each characteristic peak for -OH group decreases significantly, which will also decrease. Secondly, the annealing temperature has a direct effect on the formation of SnO₂ nanocrystals. Figure.10 shows the XRD results of samples containing 15% Sn⁴⁺ annealed at different temperatures. When annealed at 400 °C, there is no obvious SnO₂ characteristic peak(JCPDF NO.41-1445). The corresponding characteristic peaks of SnO₂ appear at 600 °C and 800 °C. However, the corresponding SnO₂ nanocrystals with a size of tens of nanometers are not suitable for energy transfer. When the annealing temperature reaches 1000 °C, the diameter of SnO₂ nanocrystals is about 3.7 nm. The energy level of quantum dots overlaps with the intrinsic excitation lines of rare earth (as shown in Fig. 2 (b)), and energy transfer occurs.

4. Conclusions

In summary, amorphous silica thin films co-doped with Tb³⁺, Ce³⁺ ions and size-tunable SnO₂ nanocrystals ions have been fabricated by facile so-gel method and spin-coating technique. The sensitivity of Ce³⁺ to Tb³⁺ is limited by Ce³⁺ concentration. Highly doped Ce³⁺ will produce large-sized CeO₂ when annealing in air atmosphere, and sometimes inhibit the light intensity of Tb³⁺. The sensitivity of SnO₂ to Tb³⁺ is limited by Sn⁴⁺ doping concentration and annealing temperature. The results show that when annealed at 1000 °C, the sensitization effect of Sn⁴⁺ (The diameter of SnO₂ is about 3.7nm) is the best. However, when annealing temperature is reduced, nano-sized SnO₂ nanocrystals cannot be effectively generated, which is not conducive to Tb³⁺ sensitization. Finally,we hope that this can be effectively used in green light signal source for CMOS compatible sensing.

Declarations

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Author's contribution

Xin Zhang, Feng Guo and Li zhuang performed the experiment, data collection and draft writing, Xin Zhang and Xiaowei Zhang design and developed the research, revised the manuscript, Qinghui Jin performed the data analysis, graph revision. All authors were involved in manuscript writing and revising.

Conflict of interest: Not applicable

References

1. Zhang X , Lin S , Lin T , et al. Improved sensitization efficiency in Er³⁺ ions and SnO₂ nanocrystals co-doped silica thin films[J]. Physical Chemistry Chemical Physics, 2015, 17(18):11974-11980.

2. Ng W L , Lourenco M A , Gwilliam R M , et al. An efficient room-temperature silicon-based light-emitting diode.[J]. *Nature*, 2001, 410(6825):192-4.
3. Won, Rachel. Silicon Photonics Synthesizer on a chip[J]. *Nature Photonics*, 2018, 12(313),81-85
4. Hall, S, R, et al. The evolution of 'sol-gel' chemistry as a technique for materials synthesis[J]. *Materials Horizons*, 2016.
5. G. Akpan and B.H. Hameed. The advancements in sol–gel method of doped-TiO₂ photocatalysts[J]. *Applied Catalysis A: General*, 2010.
6. Rahman I A , Padavettan V . Synthesis of Silica Nanoparticles by Sol-Gel: Size-Dependent Properties, Surface Modification, and Applications in Silica-Polymer Nanocomposites—A Review[J]. *Journal of Nanomaterials*, 2012, 2012(1687-4110):8.
7. A.A. Seed Ahmed, O.M. Ntwaeaborwa, M.A. Gusowski, et al. 5D₃→7F_J emission of Tb doped sol–gel silica[J]. *Physica B Physics of Condensed Matter*, 2012, 407(10):1653-1655.
8. Morais Faustino B M , Foot P J S , Kresinski R A . Lanthanide Luminescence Sensitization via SnO₂ Nanoparticle Host Energy Transfer[J]. *Journal of Luminescence*, 2018, 206.
9. M. Ntwaeaborwa and H.C. Swart and R.E. Kroon and P.H. Holloway and J.R. Botha. Enhanced luminescence and degradation of SiO₂:Ce,Tb powder phosphors prepared by a sol–gel process[J]. *Journal of Physics and Chemistry of Solids*, 2006.
10. M. Ntwaeaborwa and H.C. Swart and R.E. Kroon and P.H. Holloway and J.R. Botha. Enhanced luminescence and degradation of SiO₂:Ce,Tb powder phosphors prepared by a sol–gel process[J]. *Journal of Physics and Chemistry of Solids*, 2006.
11. Morais Faustino B M , Foot P J S , Kresinski R A . Lanthanide Luminescence Sensitization via SnO₂ Nanoparticle Host Energy Transfer[J]. *Journal of Luminescence*, 2018, 206.
12. Zhang X , Lin S , Lin T , et al. Improved sensitization efficiency in Er³⁺ ions and SnO₂ nanocrystals co-doped silica thin films[J]. *Physical Chemistry Chemical Physics*, 2015, 17(18):11974-11980.
13. Zhang X , Lin T , Zhang P , et al. Highly efficient near-infrared emission in Er³⁺ doped silica films containing size-tunable SnO₂ nanocrystals[J]. *Optics Express*, 2014, 22(1):369-376.
14. Hau-Yun Chung, Chung-Hsin Lu, Chia-Hao Hsu. Preparation and Photoluminescence Properties of Novel Color-Tunable MgY₄Si₃O₁₃:Ce³⁺, Tb³⁺ Phosphors for Ultraviolet Light-Emitting Diodes[J]. *Journal of the American Ceramic Society*, 2010, 93.
15. Caldiño, and,el. Spectroscopic characterization and optical waveguide fabrication in Ce³⁺, Tb³⁺ and Ce³⁺/Tb³⁺ doped zinc–sodium–aluminosilicate glasses[J]. *Optical Materials*, 2011.
16. Lin, N.Wang, M.Han, J.Xu, K.-J. Chen, Synthesis, structures and luminescence properties of SnO₂ nanoparticles, *Acta Phys. Sin.* 58 (2009) 5821–5825.
17. Guodong Q , Minquan W , Mang W , et al. Structural evolution and fluorescence properties of Tb³⁺-doped silica xerogels in the gel to glass conversion[J]. *Journal of Luminescence*, 1997, 75(1):63-69.

18. Arif M , Shkir M , Alfaify S , et al. Linear and non-linear optical investigations of N: ZnO/ITO thin films system for optoelectronic functions[J]. Optics & Laser Technology, 2018, 112:539-547.
19. Venkateswarlu K , Bose A C , Rameshbabu N . X-ray peak broadening studies of nanocrystalline hydroxyapatite by Williamson–Hall analysis[J]. Physica B Physics of Condensed Matter, 2010, 405(20):4256-4261.
20. Kroon R E , Ahmed H A A S , Ntwaeaborwa O M , et al. Luminescence from Ce in sol-gel SiO₂[J]. Physica B Condensed Matter, 2012, 407(10):1595-1598.

Figures

Figure 1

Overlap region of the excitation spectrum of Tb³⁺ and the emission spectrum of Ce³⁺ for singly doped silica samples.

Figure 2

(a) Normalized emission and excitation spectra of SnO₂ nanoparticles. (b) Tb³⁺ sensitization via by defect states of the SnO₂ nanoparticles.

Figure 3

PLE spectra of samples with 4% Tb³⁺ and 15% Sn⁴⁺ detected at 542 nm.

Figure 4

PL spectra of silica thin films co-doped with different dopants under the excitation of 320 nm

Figure 5

PL spectra of different Sn⁴⁺ and 4% Tb³⁺,2%+Ce³⁺ co-doped thin film samples.

Figure 6

The XRD results of samples in different Sn⁴⁺ concentrations after 1000°C annealing.

Figure 7

PL spectra of different Ce^{3+} and 4% Tb^{3+} , 15% Sn^{4+} co-doped thin film samples.

Figure 8

The XRD results of samples in different Ce^{4+} concentrations after 1000°C annealing.

Figure 9

PL spectra of thin films with different temperature

Figure 10

The XRD results of samples containing 15% Sn⁴⁺ annealed at different temperatures