*Chem. Mater.* **2007,** *19,* 2585−2588

# Characterization and Photoluminescence Properties of Tb-Doped $SiO_2$ Nanowires as a Novel Green-Emitting Phosphor

Jing Lin, Yang Huang, Jun Zhang, Jianming Gao, Xiaoxia Ding, Zhixin Huang, and Chengcun Tang*

*College of Physical Science and Technology, Huazhong Normal University, Wuhan 430079, China*

Long Hu

*School of Materials Science and Engineering, Hebei University of Technology, Tianjin 300130, China*

Dongfeng Chen

*China Institute of Atomic Energy, Beijing 102413, People's Republic of China*

*Received January 29, 2007. Revised Manuscript Received March 12, 2007*

Tb-doped $SiO_2$ nanowires have been synthesized through a vapor−liquid−solid (VLS) mechanism. The morphology and compositional characteristics of the doped nanowires have been investigated by various microscopy techniques. The prepared nanowires have amorphous characteristics with a diameter distribution range from 15 to 30 nm and a length up to several micrometers. Photoluminescence properties of pure $SiO_2$ nanowires and Tb-doped $SiO_2$ nanowires have been investigated, respectively. It shows that pure $SiO_2$ nanowires have a broad green emission band with a maximum around 515 nm, which is related to the hydrogen-related species (≡Si−H and ≡Si−OH). While $Tb^{3+}$-doped $SiO_2$ nanowires have novel green emissions both from the doped $Tb^{3+}$ ions and the host $SiO_2$ nanowires. The relationship between the two kinds of emissions has also been investigated. These Tb-doped amorphous $SiO_2$ nanowires exhibit great potential to act as a novel green-emitting phosphor.

## 1. Introduction

Recently, inorganic optical materials in nanometer scale have become one of the current focuses in the field of modern nanoscience and nanotechnology, which could find numerous potential applications in the fields of physics, chemistry, and biology.[1,2] In particular, one-dimensional optical nanomaterials have attracted increased scientific and technological interest in the fields of localization of light, lower dimensional waveguide, and scanning near-field optical microscopy (SNOM).[3] Therefore, it is important to synthesize one-dimensional optical nanomaterials that can meet the demands of further applications. Nowadays, with the phase-pure nanowire synthesis becoming controllable, nanowire doping for desired optical properties have received more and more attention. The synthesis and optical properties of rare earth (RE) ion-doped one-dimensional nanomaterials have been investigated extensively,[4−11] exhibiting interesting photoluminescence (PL) properties.

The trivalent terbium ion ($Tb^{3+}$) is an important rare-earth dopant for green phosphors. $Tb^{3+}$-doped materials are well-known for good PL characteristics from a $^5D_4 \rightarrow {}^7F_J$ transition in the visible range.[12] Up to now, most of the investigations have focused on the crystalline materials of green phosphor, such as three commercial green phosphors, i.e., $CeMgAl_{11}O_{19}:Tb^{3+}$, $Y_2SiO_5:Tb^{3+}$, and $LaOBr:Tb^{3+}$, while the luminescence of $Tb^{3+}$-doped amorphous materials has been paid little attention. Amorphous silica ($SiO_2$) is an important PL material and the PL bands of bulk silica have peaks within 1.9−4.3 eV.[13,14] As a promising one-dimensional material, amorphous silica nanowire has been synthesized through various approaches[3,15−19] and its PL properties have also been intensively investigated. Yu et al.[3]

---

* Corresponding author. Tel.: +86-27-67861185. Fax: +86-27-67861185. E-mail: cctang@phy.ccnu.edu.cn.

(1) Justel, T.; Nikol, H.; Ronda, C. *Angew. Chem., Int. Ed* **1998**, *41*, 3084.
(2) Hebbink, G.; Stouwdam, J.; Reinhoudt, D.; Beggel, E. *Adv. Mater.* **2002**, *14*, 1147.
(3) Yu, D. P.; Hang, Q. L.; Ding, Y.; Zhang, H. Z.; Bai, Z. G.; Wang, J. J.; Zou, Y. H.; Qian, W.; Xiong, G. C.; Feng, S. Q. *Appl. Phys. Lett.* **1998**, *73*, 23.
(4) Song, H.; Yu, L.; Lu, S.; Wang, T.; Liu, Z.; Yang, L. *Appl. Phys. Lett.* **2004**, *85*, 470.
(5) Yu, L.; Song, H.; Lu, S.; Liu, Z.; Yang, L. *Chem. Phys. Lett.* **2004**, *399*, 384.
(6) Meyssamy, H.; Riwotzki, K.; Kornowski, A.; Naused, S.; Haase, M. *Adv. Mater.* **1999**, *11*, 840.
(7) Yada, M.; Mihara, M.; Mouri, S.; Kijima, T. *Adv. Mater.* **2002**, *14*, 309.
(8) Wu, C.; Qin, W.; Qin, G.; Zhao, D.; Zhang, J.; Huang, S. *Appl. Phys. Lett.* **2003**, *82*, 520.
(9) Jia, C.; Sun, L.; Luo, F.; Jiang, X.; Wei, L.; Yan, C. *Appl. Phys. Lett.* **2004**, 84, 5305.
(10) Wang, X.; Li, Y. *Chem.−Eur. J.* **2003**, *9*, 5627.
(11) Lin, J.; Huang, Y.; Zhang, J.; Song, H. S.; Elssfah, E. M.; Liu, S. J.; Luo, J. J.; Ding, X. X.; Qi, S. R.; Tang, C. C. *Appl. Phys. Lett.* **2006**, *89*, 033118.
(12) Guo, C. X.; Zhang, W. P.; Shi, C. S. *J. Lumin.* **1981**, *24−25* (Part 1), 297.
(13) Nishikawa, H.; Shiroyama, T.; Nakamura, R.; Ohki, Y. *Phys. Rev. B* **1996**, *45*, 586.
(14) Liao, L. S.; Bao, X. M.; Zheng, X. Q.; Li, N. S.; Min, N. B. *Appl. Phys. Lett.* **1996**, *68*, 850.

10.1021/cm070271+ CCC: $37.00

have pointed out the potential applications of silica nanowires in high-resolution optical heads of scanning near-field optical microscope or nanointerconnections in future integrated optical devices. However, the research of $SiO_2$ nanowires doped with $Tb^{3+}$ ions is still very limited. We assume the $Tb^{3+}$-doped $SiO_2$ nanowires to be a new type of phosphor with interesting PL properties and nanoscale characteristics. The $Tb^{3+}$ ions are doped into amorphous $SiO_2$ nanowires and form independent luminescence centers. Both doped $Tb^{3+}$ ions and host $SiO_2$ nanowires will contribute to the PL of the composite phosphor. These two kinds of luminescence will influence each other; the result in the different doping concentration makes different PL emission.

In this paper, we report the synthesis of $Tb^{3+}$-doped $SiO_2$ nanowires by a vapor−liquid−solid (VLS) mechanism. The PL properties of pure $SiO_2$ nanowires and Tb-doped $SiO_2$ nanowires have been investigated. These nanowires have novel green emissions both from doped $Tb^{3+}$ ions and host $SiO_2$ nanowires. The relationship between the two kinds of emissions has also been investigated. The synthesized composite nanowires may find potential applications as a new type of green-emitting phosphor due to their novel PL characteristics and nanoscale properties.

## 2. Experimental Section

We use a Si−Fe−Tb alloy for the starting reactant to prepared Tb-doped Si nanowires. Si is the source of $SiO_2$, and Fe is used as catalyst metal.[20] The small quantity of Tb is dopant. The Si−Fe−Tb alloy with molar ratio of 1:0.1:0.04 was prepared in a vacuum arc furnace previously. The prepared alloy was grinded down and ball-milled for 8 h. Then the milled powder was placed in an alumina crucible followed by transference into the alumina tube mounted in the tube furnace. There was a water-cooled copper bar located about 10 cm downstream from the alumina crucible. The tube was first flushed with argon gas, and then an ambient mixture of argon and hydrogen was flowing through the tube during the whole reaction period to prevent the oxidation of $Tb^{3+}$. The furnace was heated to 1210 °C for 3 h and then cooled to room temperature. After the reaction, the resultant product was typically obtained as a gray layer in the crucible.

The product morphology was examined by scanning electron microscopy (SEM, JEOL, JSM-6700F). The sample powder containing a one-dimensional nanostructure, as revealed by SEM, was further ultrasonically dispersed in a $CCl_4$ solution and dropped onto a carbon-coated copper grid. Transmission electron microscopy (TEM, JEOL, JEM-100cxII, JEM-300F) was performed at 300 kV. Energy dispersive spectroscopy (EDS) was utilized for the elemental composition analysis of the one-dimensional nanostructures. The PL spectra of the gray powder was measured at room temperature in the spectral range from 350 to 750 nm using a He−Cd laser as the excitation source with a wavelength $\lambda_{exc} = 325$ nm.

## 3. Results and Discussion

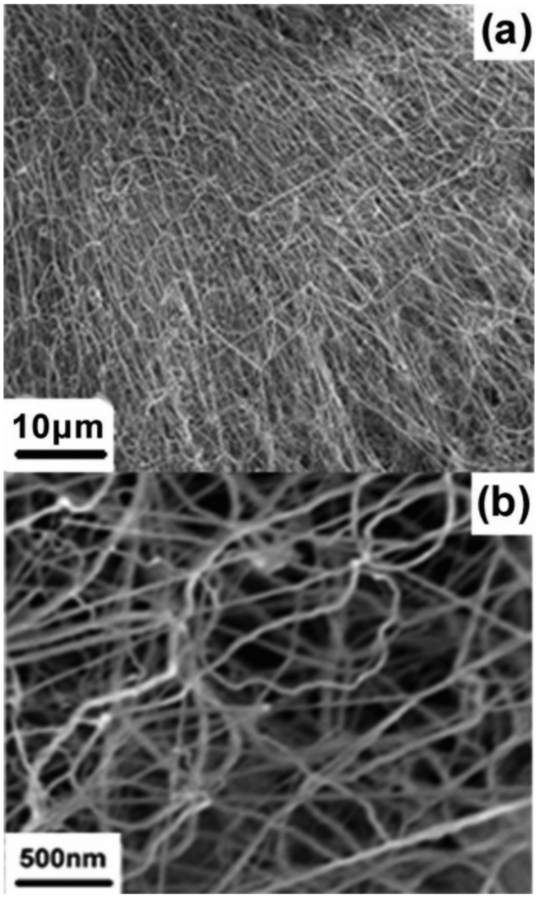

**Figure 1.** SEM image of the general morphology of Tb-doped $SiO_2$ nanowires.

The morphology of the synthesized Tb-doped $SiO_2$ nanowires is shown in Figure 1. The low-magnification image (Figure 1a) clearly reveals the product consists of a high yield of interwoven nanowires. The high-magnification image (Figure 1b) depicts the detail morphology of the nanowires. The flexural nanowires have diameters of several tens of nanometers and a typical length of several micrometers.

Figure 2 shows a typical TEM image of the synthesized composite nanowires. It is clear to observe that the nanowires have a diameter distribution range from 15 to 30 nm and the contrast for each nanowire is uniform, without any impurities. Besides, almost all of the nanowires are tipped with a nanoparticle, respectively, as shown in Figure 2a by arrows. This typical morphology has proved that the growth of the nanowires should be dominated by a VLS mechanism.[21,22] According to the Fe−Si phase diagram, there is a eutectic formed at 1207 °C. Therefore, Si and Fe formed liquid alloys when the reaction temperature reached 1210 °C, which was above the eutectic point. Once the liquid droplet was supersaturated with Si, nanowire growth started to occur at the solid−liquid interface. At the high reaction temperature, Si was oxidized into $SiO_2$ and Tb was doped into the nanowire due to thermal diffusion, obtaining Tb-doped $SiO_2$ nanowires. The EDS of the nanoparticle (Figure 2b, inset) shows it mainly consists of Si, Fe, and a little O. The SAED patterns performed on the nanowire indicate its

---

(15) Wang, Y. W.; Liang, C. H.; Meng, G. W.; Peng, X. S.; Zhang, L. D. *J. Mater. Chem.* **2002**, *12*, 651.
(16) Kar, S.; Chaudhuri, S. *Solid State Commun.* **2005**, *133*, 151.
(17) Jiang, Z.; Xie, T.; Yuan, X. Y.; Geng, B. Y.; Wu, G. S.; Wang, G. Z.; Meng, G. W.; Zhang, L. D. *Appl. Phys. A* **2005**, *81*, 477.
(18) Pan, Z. W.; Dai, Z. R.; Ma, C.; Wang, Z. L. *J. Am. Chem. Soc.* **2002**, *124*, 1887.
(19) Zheng, B.; Wu, Y.; Wang, P.; Liu, J. *Adv. Mater.* **2002**, *14*, 122.
(20) Morales, A.; Lieber, C. *Science* **1998**, *279*, 208.
(21) Xia, Y. N.; Yang, P. D.; Sun, Y. G.; Wu, Y. Y.; Mayers, B.; Gates, B.; Yin, Y. D.; Kim, F.; Yan, H. Q. *Adv. Mater.* **2003**, *15*, 353.
(22) Huang, Y.; Lin, J.; Zhang, J.; Ding, X. X.; Qi, S. R.; Tang, C. C. *Nanotechnology* **2005**, *16*, 1369.

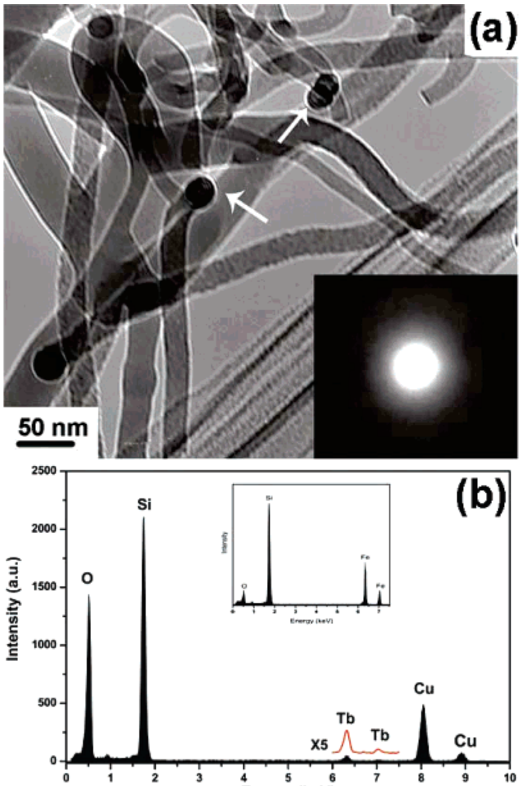

**Figure 2.** (a) Typical TEM image of Tb-doped $SiO_2$ nanowires, showing the detail morphology and uniform diameter. The corresponding SAED pattern (inset) revealing amorphous characteristics of the nanowire. (b) EDS spectrum taken from a single nanowire. (Inset) EDS spectrum taken from a nanoparticle at the end of a nanowire.

amorphous characteristic (Figure 2a, inset). To confirm the chemical stoichiometry and the successful doping of the synthesized nanowires, we performed EDS on a single nanowire. Taken from the different positions in the nanowire, we obtained the similar Tb doping with the same concentration. Figure 2b shows that the nanowire is mainly composed of Si and O (the copper signal is due to the carbon-coated copper grid used as a sample holder), and the atomic ratio of Si:O is about 1:2, indicating the composition of the nanowire is $SiO_2$. Besides Si and O, Tb was also detected in the single nanowire, indicating that Tb had been successfully doped into the nanowire.

We first investigate the PL properties of pure amorphous $SiO_2$ nanowires without doping. The synthesized method is the same as the above process except for the addition of Tb into the starting reactant alloy. Figure 3a shows the corresponding emission spectrum. It presents a broad band with a maximum around 515 nm (∼2.4 eV) and a number of shoulders between 400 and 460 nm. For bulk amorphous silica, the 459 nm (∼2.7 eV) band is ascribed to the neutral oxygen vacancy ($\equiv$Si$-$Si$\equiv$) and the 413.3 nm (∼3 eV) band is due to some intrinsic diamagnetic defect centers, such as the twofold coordinated silicon lone pair centers.[23−25] These defects are due to oxygen deficiency in the sample. Besides, the green PL band in silica nanoparticles peaked at ∼2.4 eV has been investigated by Glinka and co-workers.[26,27] They concluded the 2.4 eV band was related to the hydrogen-related species. Nanoscaled $SiO_2$ usually has a large concentration of structural defects ($\equiv$Si$\bullet$ and $\equiv$Si$-$O$\bullet$), resulting from the $\equiv$Si$-$O$-$Si$\equiv$ bond splitting at the moment of nanowire formation. However, the impurities, especially hydrogen with a small radius, normally block these defects and form hydrogen-related species ($\equiv$Si$-$H and $\equiv$Si$-$OH). The $\equiv$Si$-$H species in the nanoscaled silica emit light in the green spectral range.[26,27] Therefore, we can attribute the green PL band of the pure amorphous $SiO_2$ nanowires to be related to the hydrogen-related species.

Figure 3b shows the PL spectrum of Tb-doped amorphous $SiO_2$ nanowires. There are four PL peaks between 450 and 650 nm. The peaks at 491, 591, and 624 nm correspond to $^5D_4 \rightarrow {}^7F_J$ ($J$ = 6, 4, and 3), respectively, while the two very strong emissions with maxima at 542 and 549 nm are most likely to be a split of the peak corresponding to $^5D_4 \rightarrow {}^7F_5$, which is ascribed to Stark splitting. The emission of $^5D_4 \rightarrow {}^7F_5$ results in a strong green light emission, even visible with the naked eye. These emission bands show inhomogeneous broadening characteristics compared with other $Tb^{3+}$-doped crystalline materials, revealing that $Tb^{3+}$ ions were doped into amorphous phase.

The peaks attributed to the emission from $^5D_3$ level to lower $^7F_J$ levels are usually observed in other $Tb^{3+}$-doped materials, while these peaks are absent in our PL spectrum. It is likely due to the cross relaxation between the neighboring $Tb^{3+}$ in the $SiO_2$ nanowires. Actually, $Tb^{3+}$ has a relatively simple 4f-configurational energy level structure: low-energy states $^7F_J$ ($J$ = 6,...,0) and excited states $^5D_3$ and $^5D_4$. The energy mismatch between $^5D_3$ to $^5D_4$ level and $^7F_0$ to $^7F_6$ level for each $Tb^{3+}$ is very small. With a very low concentration of $Tb^{3+}$, the transitions of $^5D_3 \rightarrow {}^7F_J$ dominate and produce the blue emissions.[28] However, as the $Tb^{3+}$ concentration reaches a high value, energy will be easily exchanged between an excited ion in the $^5D_3$ state and a second ion in the ground state $^7F_6$ and cross relaxation is likely to take place.[29] Then the emissions from $^5D_3$ to $^7F_J$ almost tend to disappear and the emissions from $^5D_4$ to $^7F_J$ dominate. According to the literature,[30] saturation becomes noticeable at about 1 atom % Tb. Our sample with Tb concentration of 4% favors the cross relaxation. The cross relaxation process represses the emissions from the $^5D_3$ level, but favors the green emissions from the $^5D_4$ level.

Besides the $Tb^{3+}$ emissions, we also observed a broad weak background band, as shown in the Figure 3b by red dashes. It can be concluded to be the PL of the host material, i.e., amorphous $SiO_2$ nanowires. Compared with Figure 3a, the PL of $SiO_2$ has been suppressed obviously, and the main

---

(23) Nishikwa, H.; Shiroyama, T.; Nakamura, R.; Ohki, Y. *Phys. Rev. B* **1992**, *45*, 586.

(24) Liao, L. S.; Bao, X. M.; Li, N. S.; Min, N. B. *Appl. Phys. Lett.* **1996**, *68*, 850.

(25) Tohmon, R.; Mizuno, H.; Ohki, Y.; Sasagane, K.; Nagasawa, K.; Hama, Y. *Phys. Rev. B* **1989**, *39*, 1337.

(26) Glinka, Y. D.; Lin, S. H.; Chen, Y. T. *Appl. Phys. Lett.* **1999**, *75*, 778.

(27) Glinka, Y. D. *Zh. Eksp. Teor. Fiz.* 1997, *111*, 1748; *JETP* **1997**, *84*, 957.

(28) Robbins, D. J.; Cockayne, B.; Lent, B.; Glasper, J. L. *Solid State Commun.* **1976**, *20*, 673.

(29) van der Weg, W. F.; Popma, Th. J. A.; Vink, A. T. *J. Appl. Phys.* **1985**, *57*, 5450.

(30) Amekura, H.; Eckau, A.; Carius, R.; Buchal, Ch. *J. Appl. Phys.* **1998**, *84*, 3867.

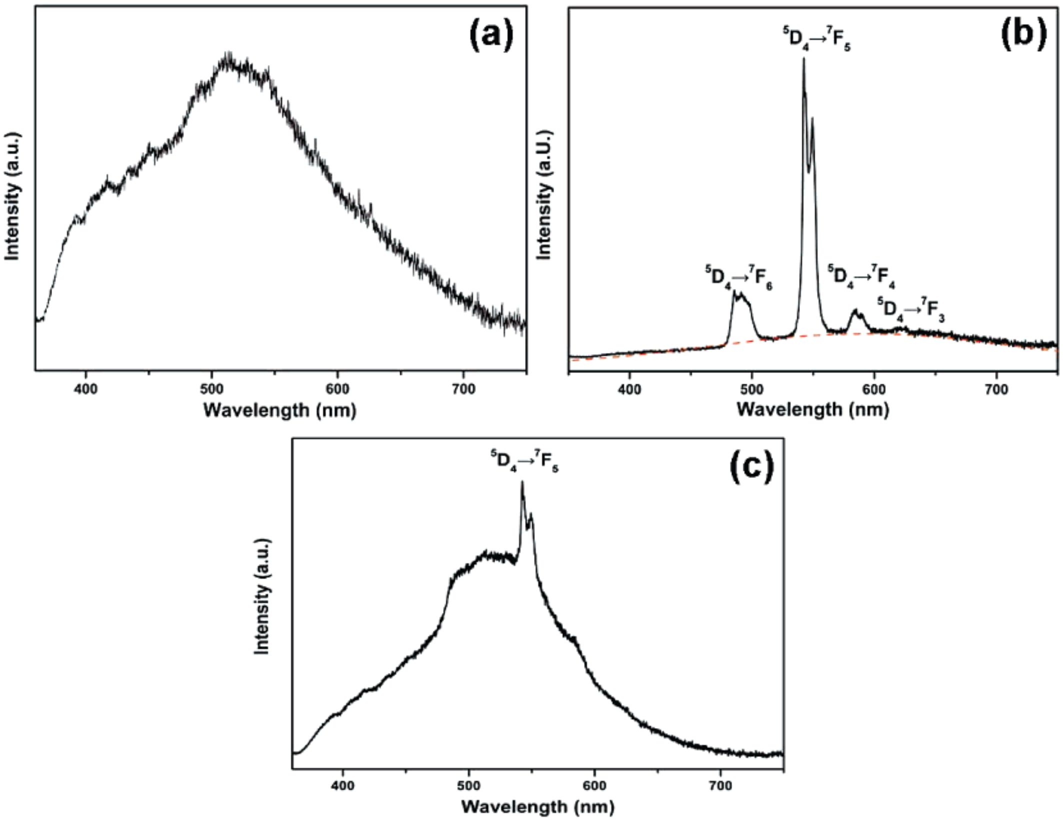

**Figure 3.** (a) PL spectrum of pure $SiO_2$ nanowires. (b) PL spectrum of 4% Tb-doped $SiO_2$ nanowires. (c) PL spectrum of 2% Tb-doped $SiO_2$ nanowires. ($\lambda_{exc} = 325$ nm).

PL is from $Tb^{3+}$. We attribute this phenomenon to being related to the high Tb-doping concentration. During the synthesized process, $Tb^{3+}$ ion is situated in a distorted cube with eight nonbridging oxygens belonging to the corners of $SiO_4$ forming tetrahedral.[31] Therefore, doping of Tb into the $SiO_2$ host forms (Si−O)−Tb bonds. With relatively high doping concentration, the number of (Si−O)−Tb bonds increases, while the number of Si dangling bonds decrease simultaneously, which result in the reduction of the hydrogen-related species (≡Si−H and ≡Si−OH). As a result, the intensity of the emission of $SiO_2$ nanowires is remarkably suppressed. To further illuminate the relationship between the two kinds of emissions, we also synthesized Tb-doped $SiO_2$ nanowires with 2% concentration and investigated the PL spectrum. Figure 3c shows a broad band between 350 and 750 nm and two narrow peaks at 542 and 549 nm. According to the analysis above, we attribute the broad band to the PL of amorphous $SiO_2$ nanowires and the two narrow peaks to the PL of doping Tb ions. Compared with Figure 3b, the PL intensity of $SiO_2$ is relatively higher and the broad band covers the $^5D_4 \rightarrow {}^7F_J$ ($J = 6$, 4, and 3) emission peaks of $Tb^{3+}$ completely. The reason is that low Tb concentration makes (Si−O)−Tb bonds decrease and the hydrogen-related species (≡Si−H and ≡Si−OH) increase relatively. The relative intensity of the two kinds of emissions are attributed to the relative concentration of hydrogen-related species and (Si−O)−Tb bonds, respectively; they influence each other. With an appropriate doping concentration (2%), the composite nanowires show the main green emission from both $Tb^{3+}$ and $SiO_2$ nanowires, exhibiting novel PL properties. We have also investigated the Tb 0.5% concentration condition and obtained the only broad PL band from $SiO_2$ nanowires. The emission peaks of Tb are overlaid by the broad band of $SiO_2$ due to the relative low doping concentration.

## 4. Conclusion

In summary, $Tb^{3+}$-doped amorphous $SiO_2$ nanowires have been synthesized through a VLS mechanism. SEM, TEM, SAED, and EDS techniques were used to characterize morphology and composition of the doped nanowires. The pure $SiO_2$ nanowires have a broad green emission band which is related to the hydrogen-related species. The PL spectrum of 4% Tb-doped $SiO_2$ nanowires shows the main emission peaks of $Tb^{3+}$ and a weak background band of $SiO_2$. The 2% Tb-doped $SiO_2$ nanowires have novel PL emissions both from the doped $Tb^{3+}$ ions and the amorphous $SiO_2$ nanowires. The study of these novel composite nanowires is of profound importance for the new applications of green-light-emitting phosphors.

**Acknowledgment.** This work was supported by the Fok Ying Tong Education Foundation (Grant No. 91050) and NNSF of China (Grant No. 50202007).

CM070271+

---

[31] Qian, G. D.; Wang, M. Q.; Wang, M.; Fan, X. P.; Hong, Z. L. *J. Lumin.* **1997**, *75*, 63.