Bright blue photoluminescence from a mixed tin and manganese oxide xerogel prepared via sol–hydrothermal–gel process*

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A new blue photoluminescent material, a mixed tin and manganese oxide xerogel, is prepared via sol–hydrothermal–gel process assisted by citric acid. The composition xerogel exhibits strong blue emission at room temperature, with an emission maximum at 434 nm under short (234 nm) or long-wavelength (343 nm) ultraviolet excitation. The photoluminescent excitation spectrum of the mixed tin and manganese oxide xerogel, monitored at an intensity maximum wavelength of 434 nm of the emission, consists of two excitation peaks at 234 nm and 343 nm. With heat treatment temperature increasing from 110 °C to 200 °C, the blue emission intensity increases remarkably, whereas it is almost completely quenched after being treated at 300 °C. The carbon impurities in the mixed tin and manganese oxide xerogel, confirmed by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy, should be responsible for the bright blue photoluminescence.

Keywords: xerogel, photoluminescence, hydrothermal, sol–gel

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1. Introduction

The blue colour is crucial to full-colour display and lighting technologies so the development of blue light luminescent materials with highly emissive, stable, and less toxic characteristics has been of great significance and interest for both the technological applications and fundamental understanding. GaN has been studied extensively as a candidate material for blue emitting diodes, but it is difficult to synthesize and expensive.[1−4] During the past years the discovery of blue luminescent porous silicon (PS)[5−8] and other important silicon oxide materials[9−17] have greatly stimulated the interest in optoelectronics and much progress has been achieved. These materials, however, suffer from some limitations for practical application, such as poor stability and aging effect, because their photoluminescence (PL) properties depend on the ambient environment and the storage condition. Nowadays, the blue photoluminescence properties of silica xerogel are also an important research subject. Highly emissive blue PL of silica xerogel prepared from an alkoxysilane and a variety of organic carboxylic acids by sol–gel method have been reported.[9,10,16,18−25] For silica xerogel materials, intentionally doped carbonyl chromophores are believed to be responsible for the photoluminescence.[24,25] However, the physical origin of the blue emission is still unclear and a matter of controversy. Up to now, the PL emission investigation of xerogel focuses on silica, but the PL emission properties of other inorganic xerogels have not been reported.

In this work, a new blue light PL emission material, a mixed tin and manganese oxide xerogel, is prepared via sol–hydrothermal–gel process, followed by heat treatment at 200 °C in air. The obtained

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manganese oxide and tin oxide composition xerogel exhibits strong blue emission, with an emission maximum at 434 nm at room temperature under short (234 nm) or long-wavelength (343 nm) ultraviolet excitation.

2. Experimental procedures

2.1. Synthesis of samples

$SnCl_4{\cdot}5H_2O$ and $MnCl_2{\cdot}6H_2O$ were used as Sn and Mn sources, respectively. Firstly, citric acid was added to 100 ml of H_2O at 50 °C until the pH reached 1.5 with magnetic stirring. After that, 8.750 g $SnCl_4{\cdot}5H_2O$ and 4.950 g $MnCl_2{\cdot}6H_2O$ were added and dissolved in the above solution. Secondly, 10-ml polyglycol (10%) was added into the above solution and stirred for 10 min, and 30-ml $NH_3{\cdot}H_2O$ (17 M) was then added dropwise to the above sol in 20 min under magnetic stirring. The hydrolysis product was stirred for 30 min to form a brown sol. The sol was transferred into a Teflon-lined autoclave for hydrothermal reaction at 150 °C for 12 h. After that, a transparent blue gel was produced. Finally, the transparent gel was dried at 110 °C for 10 h, and treated at 200 °C in air for 1 h to obtain a mixed tin and manganese oxide xerogel. The mole ratios of Sn and Mn were 75 : 25, 50 : 50, and 25 : 75, respectively, and according to the mole ratio of Sn and Mn, the samples were labeled as Sn75Mn25, Sn50Mn50, and Sn25Mn75, respectively. The Sn50Mn50 was also prepared without the citric acid to understand the effect of citric acid.

2.2. Characterization of samples

The crystalline phase was determined by X-ray diffraction (XRD, Cu$K\alpha$, 40 kV, 60 mA, Rigaku D/max-2400). The chemical bond information was collected by Fourier transform infrared spectroscopy (FT-IR) spectra (Nicolet 560 spectrometer). The chemical composition and the charge state were determined by a KRATOS XSAM 800 X-ray photoelectron spectrometer (XPS) with monochromatic Al$K\alpha$ ($hv = 1486$ eV) radiation for elemental analysis. The ultraviolet-visible (UV-Vis) absorption and PL spectra were recorded by Shimadzu UV-2550 and RF-5301PC spectrophotometers, respectively.

3. Results and discussion

The PL spectra of the mixed tin and manganese oxide xerogel under excitation with 350-nm light at room temperature are illustrated in Fig. 1. Long wavelength ultraviolet excitation (350 nm) results in a characteristic broad intense blue luminescence with an emission maximum at 434 nm. The observed emission is quite stable and shows no aging effects after exposure to the ambient environment for more than 12 months. It can also be seen from Fig. 1 that the blue luminescence intensity of Sn50Mn50 xerogel is the highest, and the peak position and the range are invariable at different ratios of Sn to Mn. It means that the three blue emissions of mixed tin and manganese oxide xerogels should originate from the same mechanism. In contrast, the blue luminescence does not appear for the Sn50Mn50 xerogel prepared without citric acid as shown in Fig. 1.

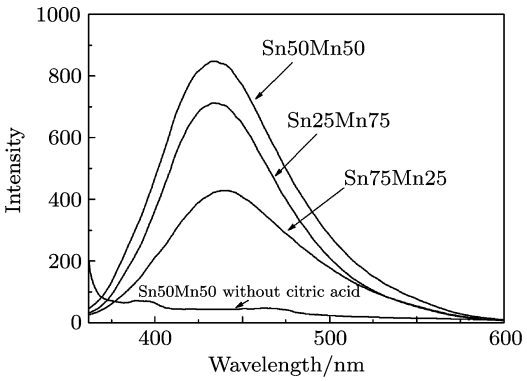


Fig. 1. PL spectra of different mixed tin and manganese oxide xerogels at room temperature (350-nm excitation).

For the Sn50Mn50 xerogel, it is observed from the PL spectra under excitation at different wavelengths (Fig. 2) that the room temperature PL spectra are excitation wavelength-dependent, and the variety of emission peak and intensity can be divided into two categories. For short excitation wavelengths of 234 nm and 275 nm (5.30 eV and 4.51 eV) (Fig. 2(a)), the emission peaks are centred at 440 nm and 445 nm (2.82 eV and 2.79 eV), respectively. The emission intensity decreases with the increase of excitation wavelength, while for long excitation wavelength from 325 nm to 400 nm (3.82 eV to 3.10 eV), (Fig. 2(b)), the broad emission band appears from 428 nm to 469 nm (2.90 eV to 2.64 eV). A red-shift of the emission peak is observed as the excitation energy decreases. The strong dependence of emission energy on the excitation wavelength indicates that the blue PL band of the

mixed tin and manganese oxide xerogel should result from a disordered-related process which is generally associated with transitions occurring within localized states in noncrystalline structures.

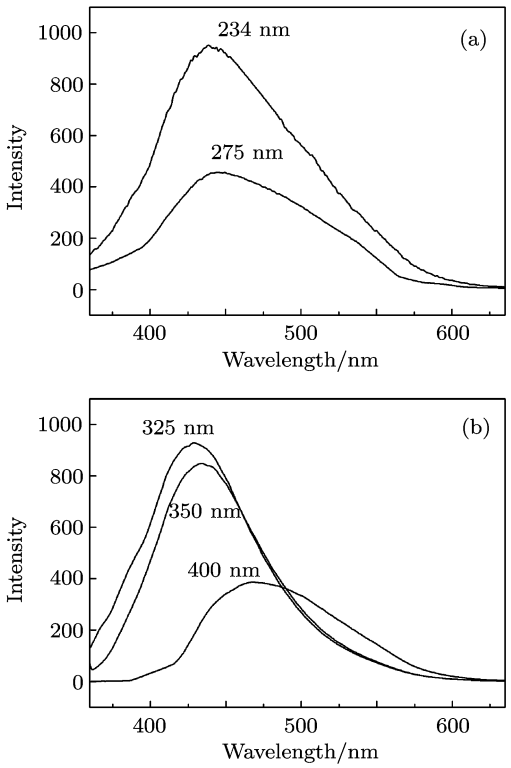


Fig. 2. PL spectra at room temperature of Sn50Mn50 xerogel at different excitation wavelengths: (a) short excitation wavelength and (b) long excitation wavelength.

Optical absorption measurement for the Sn50Mn50 xerogel confirms that the optical band gap is about 234 nm and 343 nm (Fig. 3). Figure 4 shows the PL excitation (PLE) spectrum of the Sn50Mn50 xerogel, monitored at the maximum intensity wavelength of 434 nm of the emission. The excitation spectrum consists of two excitation bands around 234 nm and 343 nm, which is consistent with the absorption spectrum (Fig. 3) and PL spectra (Fig. 2). Thus, the Sn50Mn50 xerogel exhibits very large Stokes shifts, 0.76 eV and 2.44 eV, between the absorption and emission of a specific band. The Stokes shift characterizes the energy relaxation between the excitions that takes place within an inhomogeneously broadened absorption line and inhomogeneous broadening may originate from interfacial roughness, defects, impurities, and other structural imperfection. In this work, carbon impurity-related defects are quite likely to be present due to the formation of carbon impurities in the defective oxide matrix.

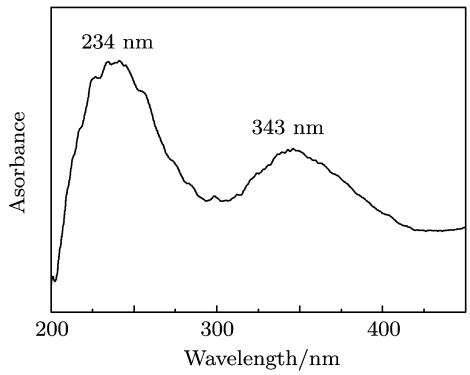


Fig. 3. Absorption spectrum of Sn50Mn50 xerogel.

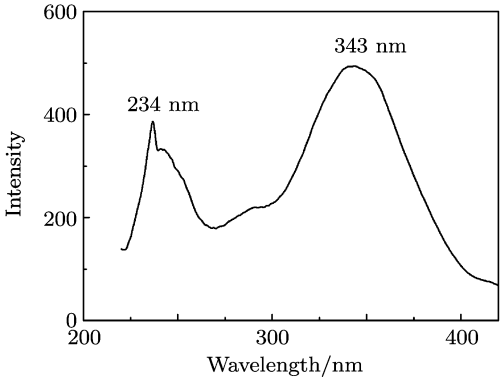


Fig. 4. PL excitation (PLE) spectrum of Sn50Mn50 xerogel, monitored at 434 nm.

Figures 2 and 4 indicate that the mixed tin and manganese oxide xerogel materials can not only convert short-wavelength UV light into visible light, but also convert long-wavelength UV light into visible light. Nowadays, the short-wavelength UV light of mercury vapour plasma is commonly used as an excitation source in the majority of commercially available lamps. Nevertheless, the usage of mercury vapour has been regarded as giving rise to environmental contamination. Thus the mixed tin and manganese oxide xerogel is potentially a less toxic alternative to the mercury currently used in fluorescent lamps.

Figure 5 shows a comparison of the PL spectra at room temperature of Sn50Mn50 xerogel treated from 110 °C to 300 °C excited by 234 nm and 350 nm, respectively. It is shown that the emission intensity increases remarkably when the heat treatment temperature is 200 °C, but the emission wavelength range remains unchanged. It indicates that the number of emission centres increases in the xerogel after curing treatment at 200 °C and the property of the emission centre does not change. The results suggest that the blue emission from the OH groups adsorbed on the surface of xerogel can be eliminated in this study,

because the OH group centre should decrease with increasing treated temperature. However, the PL emission is almost completely quenched after curing at a treatment temperature of 300 °C. The reduction of emission intensity at 300 °C should be due to the disappearance of emission centres.

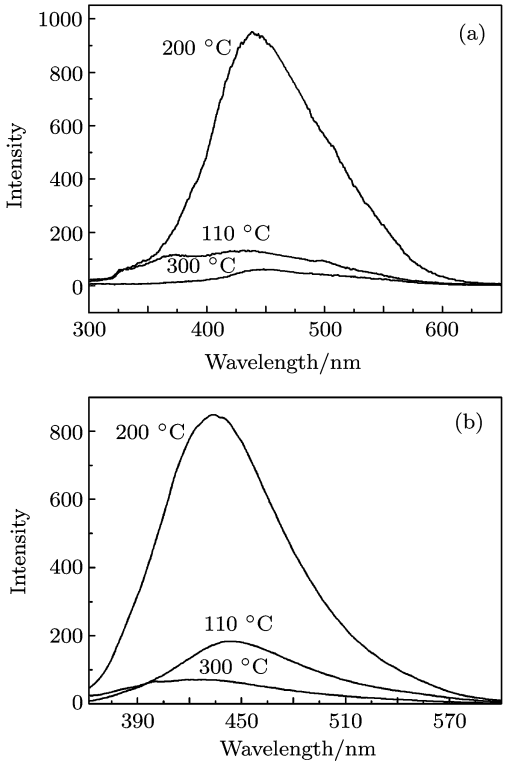


Fig. 5. PL spectra at room temperature of the Sn50Mn50 xerogel treated at different temperatures: (a) under 234-nm excitation (b) under 350-nm excitation.

Tin oxide compounds or manganese oxide compounds do not emit luminescence or show weak blue luminescence derived from the defect of crystalline structures. The physical origin of the blue PL band in the mixed tin and manganese oxide xerogel has not been unambiguously clarified, but it is quite likely that C- or OH-related surface defects play a crucial role, either directly or indirectly, in exhibiting the blue PL band. The blue PL increase in the xerogel treated from 100 °C to 200 °C proves that it should not result from the OH groups. Alternatively, this emission of the xerogel may originate from the possible carbon impurity mechanism. The origin of carbon impurity can be investigated from the synthesis process.

For the formation of the mixed tin and manganese oxide xerogel, the hydrothermal process is crucial. The hydrothermal method has been widely used to prepare a variety of powders with diversified structures.[26−28] However, the gel from the hydrothermal process has not been reported, which is often prepared by sol–gel technology. In general, the materials synthesized from $SnCl_4{\cdot}5H_2O$ or $MnCl_2{\cdot}6H_2O$ with $NH_3{\cdot}H_2O$ are $Sn(OH)_4$ and $Mn(OH)_2$, and they are converted into SnO_2 or MnO powders by forming the Sn–O–Sn or Mn–O–Mn bonds in hydrothermal process, respectively.

Under current experimental conditions, when the mole ratios between Sn and Mn range from 25 to 75 and from 75 to 25 and with citric acid assisted, a transparent gel can be obtained after hydrothermal reaction at 140 °C. Thermal treatment below 200 °C in air produces a navy blue xerogel that exhibits intense blue emission to the naked eye under UV excitation. Beyond the ratio ranges, the reaction product is powder, which could not behave as blue PL emission. The reason for the formation of a gel is that the co-existence of Sn^{4+} and Mn^{4+} and the existence of citric acid hinder the formation of tin oxide and manganese oxide, but many Sn–O–Mn networks are formed by reaction of hydrolysis with condensation of $SnCl_4{\cdot}5H_2O$ and $MnCl_2{\cdot}6H_2O$ precursors. A substantial amount of citric acid may be absorbed in the gel as a citrate species (typically carboxylic groups) and decompose into a C substitutional defect for Sn and Mn in the hydrothermal process. The retention of organics in gel also leads to the colour of the samples.

In the present work, it is thought that the trapped carboxylic groups in the lattice lead to luminescent defect centres that are responsible for the bright blue PL. The observed Stokes shift is also a strong indicator of carbon impurities-related defects in the mixed tin and manganese oxide xerogel, and the broad blue emission bands are most likely related to the carbon impurities. Because of the absence of carboxylic groups, the sample prepared without citric acid does not show the blue luminescence (Fig. 1). A similar emission from silica xerogel has been previously reported.[16,22] The carbon impurity mechanism has been used to explain the luminescence phenomena that occurred in the system of silane coupling agents reacting with the organic acid, where the emission is considered to originate from the introduced carbon impurities in the O–Si–O network by forming O–C–O or Si–C bonds. For example, bright PL from carboxylic-doped silica xerogel has been reported by Green *et al.*,[24] and the luminescence was ascribed to carboxylic acids trapped

in silicates prepared from a silicate-carboxylate sol–gel precursor. The blue luminescence of silica xerogel is helpful to identify the source of the emission of the mixed tin and manganese oxide xerogel. The obtained PL properties of the mixed tin and manganese oxide xerogel are quite analogous to those of silica xerogel, suggesting that both PL emissions result from a similar origin of carbon impurities-related defects.

Thermal treatments can also result in the formation of various defect centres. More carboxylic groups in the xerogel decompose to create more C substitutional defects for Sn and Mn in the heating process, so when the treatment temperature increases to 200 °C, the blue emission intensity also increases (Figs. 4 and 5). However, when the treatment temperature increases up to 300 °C, the emission centre is quenched, specifically, because the carbon impurity is burned out at 300 °C.

In order to understand the details, further information about the mixed tin and manganese oxide xerogel is obtained by XRD, FT-IR, and XPS measurements. In the XRD patterns of Sn50Mn50 xerogel prepared at 100 °C (Fig. 6), the clear peaks of NH_4Cl indicate that a byproduct exists in the xerogel. When the samples are treated at 200 °C and 300 °C, the peaks of NH_4Cl disappear completely because NH_4Cl is volatilized. In addition, several broad peaks at about 26.7°, 33.8°, 51.6°, and 64.3° are also observed in the patterns, which should be ascribed to the mixed tin and manganese oxide, e.g., $MnSnO_3$. These peaks also become sharper in the patterns collected at higher temperatures. This reveals that the mixed tin and manganese oxide xerogel may have been partially crystallized at a higher temperature.

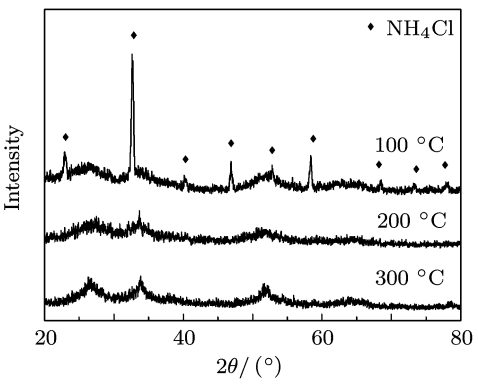


Fig. 6. XRD patterns of Sn50Mn50 xerogel treated at different temperatures.

FT-IR and XPS spectra are used to investigate the carbon impurities as shown in Figs. 7 and 8, respectively. In the transmission FT-IR spectrum, the broad absorption peaks at 3435 cm^{-1} and 1596 cm^{-1} are attributed to the stretching and bending vibration of hydroxyl, respectively. The absorption bands at 3185 cm^{-1}, 3040 cm^{-1}, 2814 cm^{-1}, and 1410 cm^{-1} region can be attributed to the presence of carbonyl impurities. Additionally, the absorption peaks at 680 cm^{-1} to 550 cm^{-1} are assigned to the asymmetric Sn–O–Sn or Mn–O–Mn stretching mode formed by condensation of adjacent surface hydroxyl groups. In the XPS spectrum (Fig. 8), the additional C (1s) peak at 284.5 eV is the criterion used to calibrate the binding energy of the peak. The C (1s) peak at 286.2 eV should originate from the C=O bonds, indicating that the carbon impurities exist in the samples.

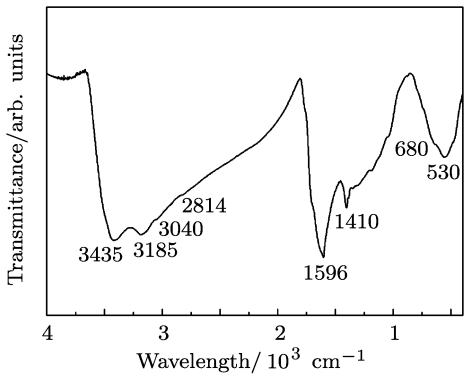


Fig. 7. Transmission FT-IR spectrum (KBr disk) of Sn50Mn50 xerogel treated at 200 °C.

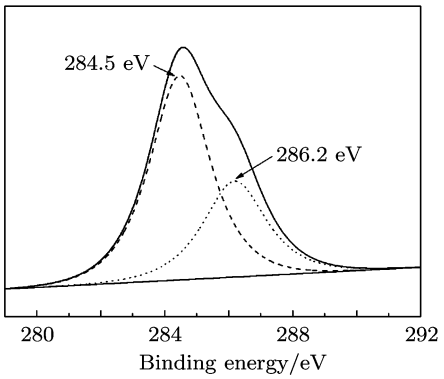


Fig. 8. XPS C (1s) peak of Sn50Mn50 xerogel treated at 200 °C.

4. Conclusions

The particular interest and importance in this work is that new PL material, the synthesized mixed tin and manganese oxide xerogel, is obtained through a sol–hydrothermal–gel process assisted by citric acid, and a bright blue PL band with an emission maximum at 434 nm at room temperature is observed

under short or long-wavelength ultraviolet excitation. The observed emission is stable after prolonged exposure to the atmosphere for more than 12 months. Although the physical origin of the blue PL emission has not been unambiguously clarified yet, it is quite likely that the carbon impurities play a crucial role, either directly or indirectly. The synthesized mixed tin and manganese oxide xerogel may thus have potential applications in full-colour display and lighting technologies.

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