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Ceramics International 31 (2005) 405–410

CERAMICS INTERNATIONAL

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Characteristics of SnO_2 annealed in reducing atmosphere

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Received 11 March 2004; received in revised form 30 March 2004; accepted 26 May 2004

Abstract

The characteristics of SnO_2 reduced in H_2/N_2 at various annealing temperatures are reported. The formation of polycrystalline metallic Sn from SnO_2 is detected by X-ray diffraction above the annealing temperature of 500 °C. The photoluminescence (PL) characteristics of reduced SnO_2 have been studied as a function of temperature. Further studies of Fourier transform infrared (FTIR), differential thermal analysis (DTA-T_g), and photoluminescence excitation (PLE) spectroscopy have been performed. Broad emission with peaks at around 590 nm (2.1 eV) and 420 nm is obtained from SnO_2. The reduced SnO_2 shows an increase PL intensity of 420 nm band. In addition the PL intensity of reduced SnO_2 at 420 nm (2.95 eV) increases with annealing in ambient air. The origin of luminescence bands detected in reduced tin oxide is discussed.

Keywords: Photoluminescence; SnO_2; XRD; FTIR; DTA

1. Introduction

Tin oxide (SnO_2), an n-type semiconductor with a wide band gap (E_g = 3.6 eV, at 300 K), is extensively used as a functional material for the optoelectronic devices [1], conductive electrodes and transparent coatings due to its good conductivity and transparency in the visible spectrum [2,3], solar cells [4,5], and catalyst support [6]. The variation of grain size, the concentration of oxygen vacancies and electrical properties of tin oxide as bulk as well as thin films are also widely studied. Along with these applications, tin oxide is an attractive material in developing solid-state sensors for reducing gases such as CO, NO, and C_2H_5OH [7–9].

Considerable efforts have been put forth to develop metal oxide semiconductor materials (SnO_2), especially the preparation of thin film and properties, which may lead to novel optoelectronic devices. The reported luminescence bands from SnO_2 are at around 2.4–2.5 eV and 2.9–3.1 eV [10–12]. The origins of these luminescence bands are not clearly understood. In general, oxygen vacancies, which usually act as radiative centers, play an important role in the luminescence properties of the metal oxide semiconductors. However, no reports exist on the luminescence properties of reduced SnO_2. Therefore, it is of interest to study the characteristics of SnO_2 in reducing atmosphere and its luminescence properties.

The characteristics of SnO_2 prepared in reducing atmosphere are analyzed through PL and PLE, XRD, FTIR, and DTA and the possible mechanism of luminescence bands are discussed.

2. Experimental

SnO_2 powders (Aldrich Chemical Co., 99.99% purity) were pressed into cylindrical pellets (1 mm thick and 5 mm in diameter) at 1000 psi, sintered at 1350 °C for 1 h under ambient air, and placed into an high purity alumina boat and reduced in H_2N_2 (5% H_2) atmosphere with a flow of 20 sccm for the duration of 1 h at various temperatures (400–630 °C). The reduction temperature above 650 °C yielded wetting and melting of SnO_2.

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doi:10.1016/j.ceramint.2004.05.026

The XRD patterns of the samples were examined using a Rigaku X-ray diffractometer with monochromatized Cu Kα radiation.

The PL equipment consists of a He–Cd laser, 50-mm collection optics, a 0.5-m scanning grating monochromator and an air-cooled GaAs photomultiplier. A long-pass filter was inserted after the sample to block any scattered laser light. The temperature dependence of PL was measured by placing the sample in the cold finger of a closed-cycle He refrigerator that allows settings between 20 K and 300 K.

For PLE measurements, a 1000 W Xe lamp was used to generate white light, which passed through a 0.15 m single grating scanning monochromator into a sample chamber. The 2 mm × 3 mm beam size of scanning light was detected by a Si detector before illuminating the sample and then the excitation spectrum was dispersed by a 0.5-m single grating monochromator. The spectrum was collected by an air-cooled GaAs photomultiplier.

The Fourier transform infrared spectra of samples were observed by diffuse reflection spectroscopy in a vacuum chamber.

3. Results and discussion

X-ray diffraction (XRD) measurements of sintered SnO_2 and reduced SnO_2 are depicted in Fig. 1. The diffraction peaks of sintered SnO_2 display a good compatibility with JCPDS 41-1445. No characteristic peaks of impurities were observed from SnO_2 sintered in air. The calculated lattice constants and unit cell volume of sintered tetragonal SnO_2 are $a = 4.733$ Å, $b = 3.184$ Å, and 71.33 Å^3, respectively, and agree to the values obtained from the JCPDS. The diffraction peaks of SnO_2 reduced in N_2 ambience exhibit the characteristics of SnO_2 with somewhat increased diffraction peak intensities and almost identical values of lattice constants and unit cell volume of SnO_2 obtained from the JCPDS. There exists two unidentified diffraction peaks at the 46.17° and 47.12°. However, the intensities of this unknown diffraction peak decrease in H_2N_2 ambient annealing with an increase of annealing temperature. The SnO_2 reduction by H_2N_2 annealing displays a general trend of lattice constants and unit cell volume to decrease. XRD diffraction patterns of reduced SnO_2 specimens in H_2N_2 also display diffraction peaks originating from polycrystalline Sn depicted as an open circle. It is generally observed that the ambient annealing of SnO_2 resulted in a gray body color above 500 °C. H_2N_2 annealing above 630 °C resulted in melting of the specimen. For Sn, a small contraction of lattice constants ($a = 5.826$ Å, $b = 3.178$ Å) compared to JCPDS 04-0673 ($a = 5.831$ Å, $b = 3.182$ Å) were observed, and resulted in a decrease of the unit cell volume (107.82 Å^3). It seems the decrease in lattice constants and unit cell volume of SnO_2 to be associated with the thermal stress and the increase of oxygen vacancies during the reduction process.

The weight loss as a function of annealing temperature is shown in Fig. 2. Initial weight loss of SnO_2 in air is relatively high up to 400 °C and then its rate decreases above 400 °C. In contrast the weight loss of SnO_2 in H_2N_2 atmosphere shows a rapid decrease above 500 °C, which is related to rapid oxygen desorption. This result agrees quite well with the XRD analysis. XRD analysis of reduced SnO_2 in H_2N_2 displays diffraction peaks originating from polycrystalline Sn above 500 °C as shown in Fig. 1.

Fig. 3 displays PL spectra of SnO_2 prepared in air (e) in N_2 atmosphere (f), and reducing H_2N_2 (a–d) atmosphere measured at room temperature. All of the measured SnO_2 PL

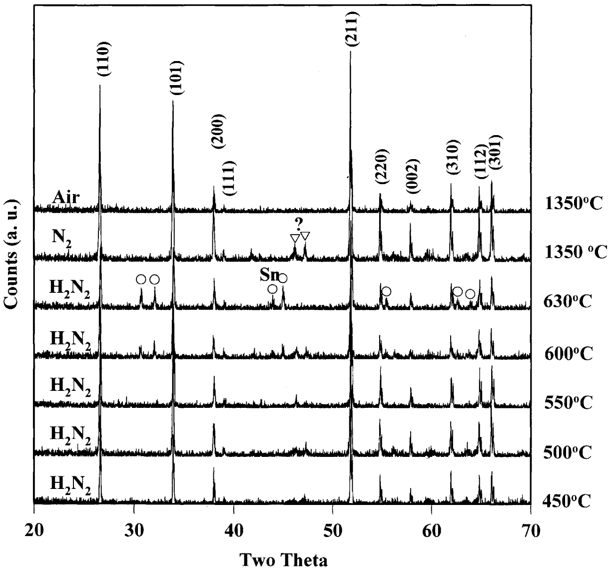

Fig. 1. XRD patterns of SnO_2 and reduced SnO_2 at various temperatures. The diffraction peaks originating from Sn are depicted as open circles.

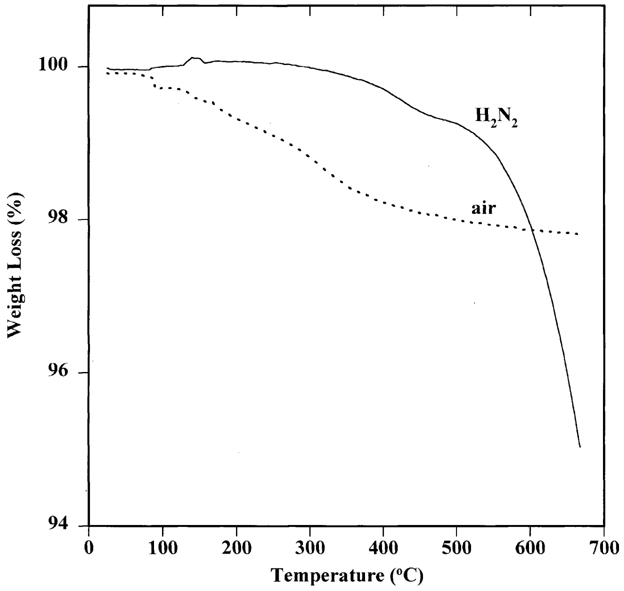

Fig. 2. The weight loss curves of SnO_2 as a function of temperatures in air and reduced H_2N_2 atmosphere.

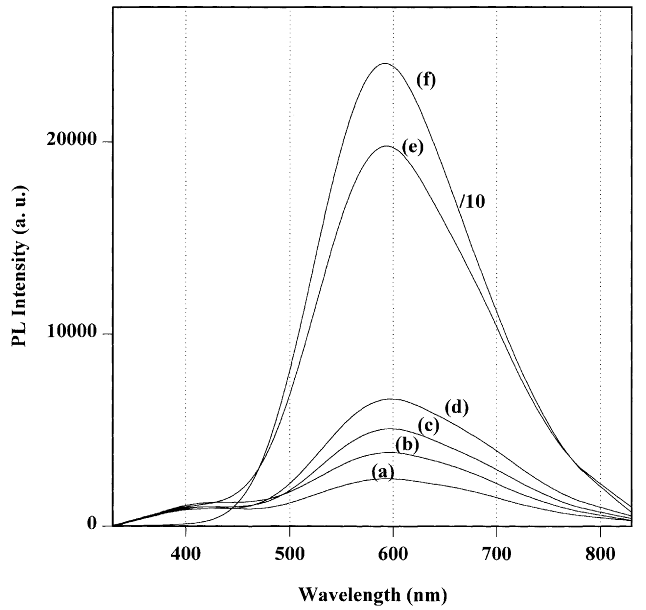

Fig. 3. Room temperature photoluminescence spectra of (a–d) sintered in N_2, and subsequently reduced H_2N_2 atmosphere. The reduced temperatures of (a–d) are 450, 550, 600, and 630 °C, respectively. The PL spectra of (e) sintered SnO_2 in air and (f) N_2 atmosphere at 1350 °C for 2 h.

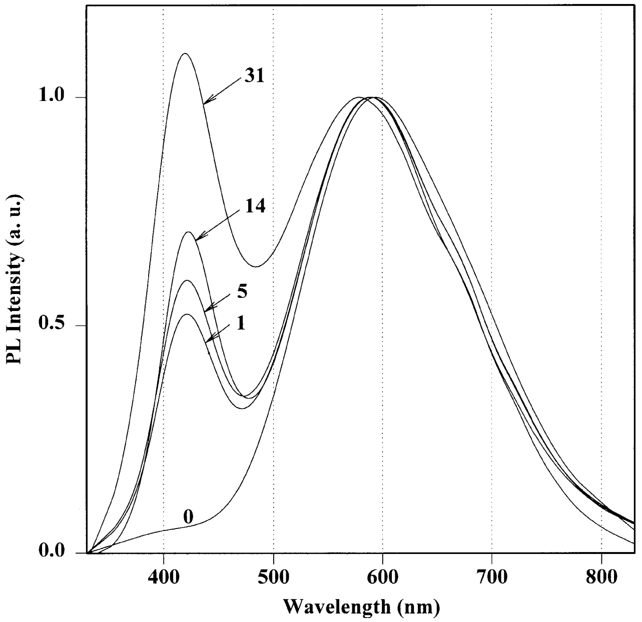

Fig. 4. Room temperature PL spectra of SnO_2 reduced in H_2N_2 at 630 °C as a function of annealing time intervals (day).

spectra are quite similar to shape and positions of PL peaks. Luminescence bands peaking at 420 nm and 590 nm have been detected. The PL intensity of SnO_2 prepared in N_2 atmosphere is one order of magnitude larger than for SnO_2 prepared in air. Thus, the reduction of SnO_2 in H_2N_2 utilized the samples prepared in N_2 atmosphere for this study. The utilization of sintered SnO_2 in ambient air does not change the result of annealing in reducing atmosphere. The intensity of 590 nm luminescence band tends to decrease with the reduction temperature from 450 °C to 630 °C (curve (a–d)). In contrast the PL intensity of 420 nm luminescence band is slightly reduced throughout H_2N_2 reduction.

Fig. 4 depicts the room temperature PL spectra of SnO_2 reduced at 630 °C with various annealing intervals (up to 31 days). The PL spectra were measured within 20 min after reduction in H_2N_2 atmosphere. The most noticeable change of PL spectra of SnO_2 is that the weak shoulder luminescence in the blue/violet spectral region of reduced SnO_2 now becomes a very pronounced peak with ambient air annealing. After 1 month of ambient air annealing of SnO_2 reduced in H_2N_2, the intensity of 420 nm and 590 nm luminescence bands are quite comparable to each other. This increase of the blue/violet luminescence band might be related to the oxidation in air atmosphere after reduction.

Fig. 5 depicts the decrease of PL intensity as a function of UV laser exposure at a power density of 1 W/cm^2. For this measurements 1-month ambient air aged SnO_2 reduced in H_2N_2 atmosphere is used. The decrease of PL intensity as a function of UV exposure is measured at the maxima of PL peak, namely 420 nm and 590 nm. Both luminescence bands display PL stability under UV exposure. The blue/violet luminescence band is a little bit more sensitive to the UV exposure.

Fig. 6 shows various PL spectra measured at selected temperatures to delineate possible similarities and differences between (a) SnO_2 prepared in N_2 at 1350 °C and (b) sintered, reduced in H_2N_2, and subsequently annealed in air for 1 month. The sintered SnO_2 exhibits a broad yellow

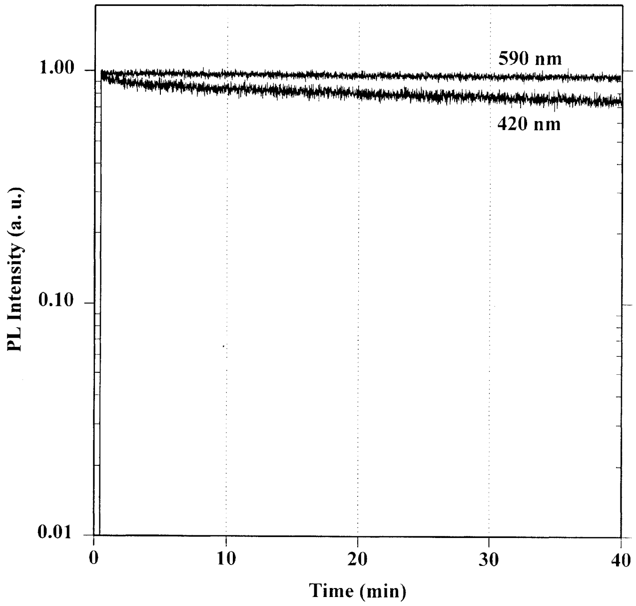

Fig. 5. The decrease of PL intensity as a function of UV laser exposure time at a power density of 1 W/cm^2. The 1-month ambience air aged SnO_2, which is reduced in H_2N_2 ambience, are used. The wavelengths are selected at luminescence peak maxima at 420 nm and 590 nm.

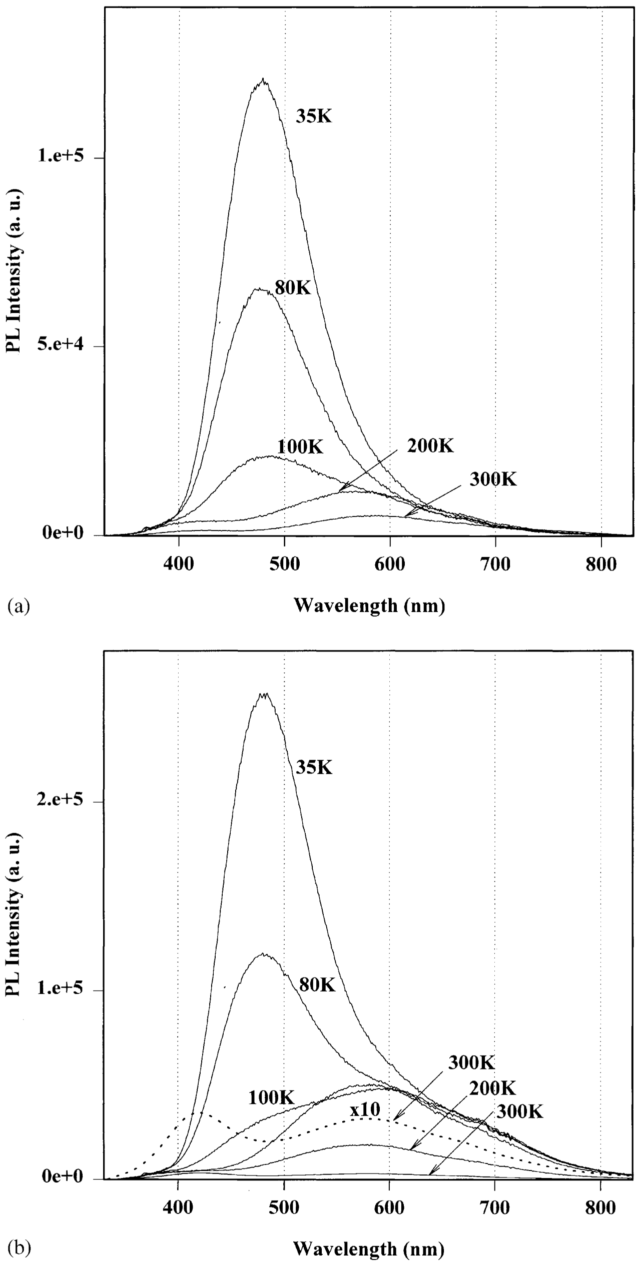

Fig. 6. PL spectra of (a) SnO_2 prepared in N_2 at 1350 °C and (b) reduced, and subsequently ambient air annealed for 1 month at some selected temperatures. Measurement temperatures are indicated.

luminescence band around 590 nm (2.1 eV) with a shoulder blue/violet luminescence band around 420 nm (2.95 eV). The sintered, reduced, and subsequently ambient annealed SnO_2 also shows a similar blue/violet and yellow luminescence band with similar PL intensities at room temperature. Initially, the yellow luminescence of both samples is shifted to 480 nm at 35 K. Further, the blue/violet luminescence at around 420 nm remains unaltered and displays the same trend as a function of temperature. Therefore, the yellow luminescence and blue/violet luminescence from sintered SnO_2 and reduced SnO_2 are associated with same origins. The semiconducting behavior of tin oxide is attributed to the presence of oxygen vacancies in the bulk lattice, which act as shallow n-type donors. The structural and electronic properties of tin oxide that stem from oxygen vacancies are critical to the electrical and optical properties [13]. It has been reported that the bridging and in-plane oxygen vacancies are characterized by occupied states higher in the band gap, which extends to the Fermi level [14]. These trapped states originating from oxygen vacancies form a series of metastable energy levels within the band gap. Thus, the observed origin of orange luminescence is probably related to a defect energy band within the band gap of SnO_2 originating from oxygen vacancies. A similar broad luminescence band at 2.4 eV is also observed from SnO_2 thin films grown by chemical vapor deposition and the origin of luminescence is assigned to oxygen vacancies [12].

It is quite interesting that the blue/violet luminescence between sintered SnO_2 and reduced SnO_2 displays a similar trend (unaltered peak positions) as a function of temperature. The blue/violet luminescence bands at 400 nm and 430 nm from SnO_2 are also reported by several researchers [10–12]. The origin of blue/violet luminescence form SnO_2 is attributed to oxygen vacancies, tin interstitial or dangling bond, and structural defects. XRD shows that the SnO_2 reduced in H_2N_2 displays polycrystalline Sn with increase of reducing temperature. Further, ambient annealing of reduced SnO_2 demonstrates the increase of blue/violet luminescence band. Thus, the origin of the blue/violet luminescence band seems to be related to Sn interstitials and nonstoichiometric oxide. As reduction temperature increase, the amount of Sn and nonstoichiometry increases with the decrease of oxygen vacancies, which result in an increase of blue/violet luminescence band with a decrease of the broad yellow luminescence. Further, ambient air annealing of reduced SnO_2 gradually increases the oxidation of Sn and passivates the surface with oxygen nonstoichiometrically, and results in an overall increase of blue/violet luminescence.

Fig. 7 shows typical photoluminescence excitation (PLE) spectra for sintered SnO_2 and reduced SnO_2 measured at the luminescence peak maxima. Curves (a and b) depict the PLE spectra of sintered SnO_2, and reduced SnO_2, respectively. The PL spectra measured at room temperature and low temperature display quite similar results, as shown in Figs. 3 and 6. Thus, it is expected that the same PLE spectra should be obtained from sintered SnO_2 and reduced SnO_2. Indeed similar shapes of PLE spectra are obtained for both samples. The reduced SnO_2 displays only the decreased the intensity of PLE spectra. A large number of absorption peaks are identified, which are measured at 420 nm. In the UV region, a strong absorption band at near 3.29 (377 nm) is detected along with a weak absorption peak at 4.66 eV (266 nm) and 3.9 eV (317 nm). The band gap of SnO_2 is 3.6 eV. Thus, any electrons pumped into excited states by a 3.82 eV (325 nm) He–Cd laser from ground state resulted in de-excitation into a 3.29 eV (377 nm) absorption band, then they revert to

2.95 eV (420 nm) via nonradiative transition, and finally return to ground state via radiative transitions. When the PLE spectra are obtained at 590 nm (2.1 eV) for sintered SnO_2 one could detect a broad absorption band from 250 nm to 400 nm and three narrow absorption bands at around 440 nm (2.82 eV), 479 nm (2.59 eV), and 525 nm (2.36 eV). At present it is difficult to assign these three narrow absorption bands, but they seem to relate to different types of oxygen vacancies and crucial to the emission of 2.1 eV. Further work is necessary to identify this.

The PL spectra of sintered SnO_2 exhibited almost identical luminescence peaks to the reduced SnO_2 in H_2N_2 ambience. Further PLE spectra of SnO_2 and reduced SnO_2 show significant similarities with respect to absorption bands. Thus, it is expected that the vibrational mode of SnO_2 and reduced SnO_2 would be quite similar. To test this, infrared vibrational spectra have been measured for SnO_2 and reduced SnO_2 and the results are shown in Fig. 8. The infrared spectra of SnO_2 and reduced SnO_2 are dominated by the vibration around 600 cm^{-1}, which is associated with an asymmetric Sn–O–Sn stretching vibrational mode [15]. It is noted that vibrational modes of SnO_2 and reduced SnO_2 are quite similar as can be seen in the figure.

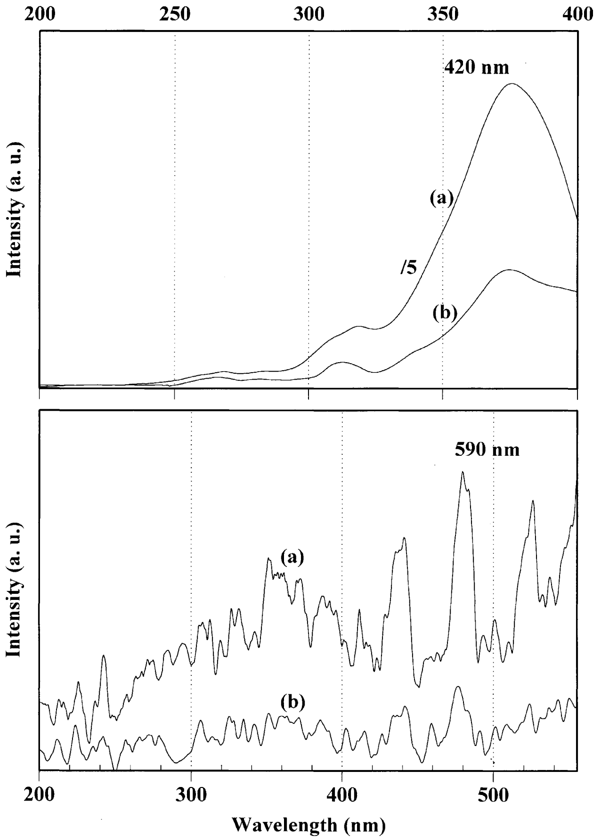

Fig. 7. PLE spectra of (a) SnO_2 prepared in N_2 at 1350 °C and (b) reduced, and subsequently ambient air annealed for 1 month. The wavelengths are selected at luminescence peak maxima at 420 nm and 590 nm.

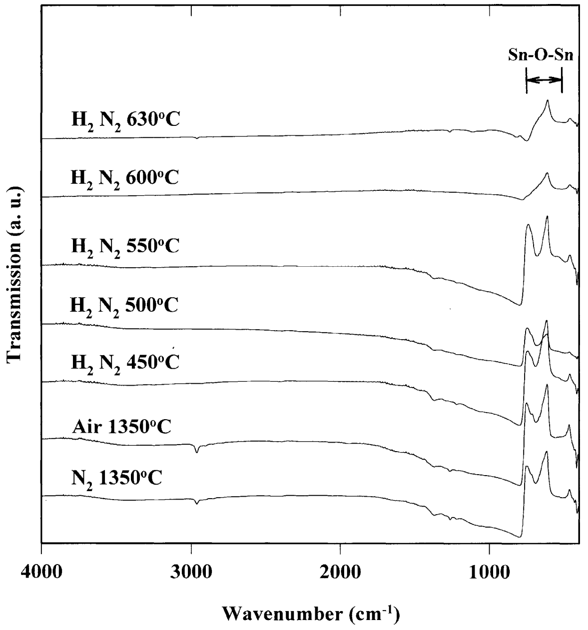

Fig. 8. Infrared vibrational spectroscopy of SnO_2 prepared in various conditions.

4. Conclusions

Polycrystalline Sn has been detected to form above 500 °C from SnO_2 reduced in H_2N_2, as demonstrated by XRD. The sintered SnO_2 and reduced SnO_2 in H_2N_2 atmosphere yield a luminescence band around 420 nm and 590 nm. The experimental results of low temperature PL and PLE measurements reveal that the origin of the luminescence band observed form SnO_2 and reduced SnO_2 is the same for each luminescence band. The blue/violet luminescence bands at 420 nm and yellow luminescence band at 590 nm are due to the Sn interstitial and nonstoichiometry and oxygen vacancies, respectively.

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